

## PATENT COOPERATION TREATY

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents  
United States Patent and Trademark  
Office  
Box PCT  
Washington, D.C. 20231  
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 11 May 2000 (11.05.00)	
International application No. PCT/GB99/02833	Applicant's or agent's file reference APB/MER/Q553
International filing date (day/month/year) 10 September 1999 (10.09.99)	Priority date (day/month/year) 11 September 1998 (11.09.98)
Applicant CHARNOCK, Peter et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:  
11 April 2000 (11.04.00)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was  
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Juan Cruz
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

PCT

REC'D 20 DEC 2000

WIPO

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference APB/MER/Q553	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/GB99/02833	International filing date (day/month/year) 10/09/1999	Priority date (day/month/year) 11/09/1998
International Patent Classification (IPC) or national classification and IPC C08G65/48		
Applicant VICTREX MANUFACTURING LIMITED et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 7 sheets, including this cover sheet.

- ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☒ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☒ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand  11/04/2000	Date of completion of this report  19.12.2000
Name and mailing address of the international preliminary examining authority:   European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized officer  O'Sullivan, T  Telephone No. +31 70 340 2795  

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/GB99/02833

**I. Basis of the report**

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).)*:

**Description, pages:**

1-45 as originally filed

**Claims, No.:**

1-35 as originally filed

**Drawings, sheets:**

1/1 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB99/02833

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

### III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

1. The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

☐ the entire international application.

☒ claims Nos. 1-35 (all in part).

because:

☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (*specify*):

☐ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. are so unclear that no meaningful opinion could be formed (*specify*):

☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.

☒ no international search report has been established for the said claims Nos. 1-35 (all in part).

2. A meaningful international preliminary examination report cannot be carried out due to the failure of the nucleotide and/or amino acid sequence listing to comply with the standard provided for in Annex C of the Administrative Instructions:

☐ the written form has not been furnished or does not comply with the standard.

☐ the computer readable form has not been furnished or does not comply with the standard.

### V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)

Yes: Claims 8-15,18,20-22

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB99/02833

---

	No:	Claims	1-7,16,17,19,23-35
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-35
Industrial applicability (IA)	Yes:	Claims	1-35
	No:	Claims	

2. Citations and explanations  
**see separate sheet**

## VI. Certain documents cited

1. Certain published documents (Rule 70.10)

and / or

2. Non-written disclosures (Rule 70.9)

**see separate sheet**

## VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

**see separate sheet**

**Re Item V**

**Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

It should be noted that the present examination refers only to that part of the present application covered by the search report(Rule 66.1 PCT) i.e. to polyaryletherketones or sulphones of the type described by the examples of the present application

D1 EP-A-0574791  
D2: WO-A-9629360  
D3: EP-A-0382440  
D4: FR-A-2748485  
D5: EP-A-0008895  
D6: EP-A-0211693

1.0 D1 concerns sulphonated polyarylether ketones and sulphones for use as polymeric electrolytes in fuel cells. Structure (II) on page 7 of D1 discloses polymers fulfilling the requirements of formula (IV) of the present application, where; E and E' are both oxygen atoms, w=1, r=0, s=1, A and B are both equal to 1, G is a direct bond, m=0 and Ar is a 1,4 phenyl group (i.e. structure (iv) in present Claim 1). Present Claims 1-7,16,19,23-31,34 are consequently not novel with respect to D1. Furthermore, given the disclosure in Claim 1 of D1 of the biphenylene group as an obvious choice for the polymers concerned, the remaining dependent claims do not contain an inventive step with respect to D1.

2.0 Similarly D2 discloses subject-matter prejudicial to the novelty of present Claims 1-7,16,19,23-31,34 and 35 and to the presence of an inventive step in the remaining claims. (see Claim 1 and Structure (III) on page 7 of D2).

3.0 Claim 1 of D3 is prejudicial to the novelty of present claims 1-7,16,17,19,23,24,25.

4.0 D4 discloses a sulphonated polymer containing the -O-biphenylene-O- unit as an ion-change polymer membrane in fuel cells.(see Claim 1 and page 16, lines 1-6 of D4).

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

---

International application No. PCT/GB99/02833

D4 is therefore prejudicial to the novelty of present Claims 1-3,19-21,23-31,35

5.0 D5 discloses a process for making polyaryletherketones and for their sulphonation which is prejudicial to the novelty of present Claims 32 and 33 (see page 4, lines 25-30 and Example 1 of D5).

6.0 D6 discloses in columns 11 and 12 many non-sulphonated polymers prejudicial to the novelty of present Claim 34.

**Re Item VI**

**Certain documents cited**

Certain published documents (Rule 70.10)

Application No Patent No	Publication date (day/month/year)	Filing date (day/month/year)	Priority date (valid claim) (day/month/year)
EP-A-0932213	28-07-99	29-12-97	29-12-97

Claims 1 and 3 of this document disclose subject-matter covering that of present Claims 1-7,16,17,18,20-35.

**Re Item VIII**

**Certain observations on the international application**

1.0 Whilst a literal support for present Claim 1 exists in the description on page 4, the application contains no technical support for the preparation of anything other than polyarylethers (more specifically polyetherketones and sulphones) There is no way of extending the particular teaching of the description to cover the potentially vast field of all polymers which contain an aromatic moiety as defined in Claim 1. Present Claim 1 must therefore be amended to make it clear that is directed solely towards said polyarylethers, polyaryletherketones and sulphones as described in the present examples (see PCT GL-IV-III-6.3).

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

---

International application No. PCT/GB99/02833

2.0 Attention is drawn to PCT Gazette, Section IV, III-4.6, concerning the non-limiting nature of the words "**preferably**" and "**preferred**" which is used throughout the description and in Claim 15. This is of particular importance with respect to the subject-matter disclosed on pages 11-13 of the present description.

4.0 The vague and imprecise statements in the description on page 29, lines 11 to 19 implies that the subject-matter for which protection is sought may be different to that defined by the claims, thereby resulting in lack of clarity (Article 6 PCT) when used to interpret them (see also the PCT Guidelines, III - 4.3a).



# PATENT COOPERATION TREATY

# PCT

09/787011

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>APB/MER/Q553</b>	<b>FOR FURTHER ACTION</b> <small>see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.</small>	
International application No. <b>PCT/GB 99/02833</b>	International filing date (day/month/year) <b>10/09/1999</b>	(Earliest) Priority Date (day/month/year) <b>11/09/1998</b>
Applicant  <b>VICTREX MANUFACTURING LIMITED et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 5 sheets.  
☒ It is also accompanied by a copy of each prior art document cited in this report.

**1. Basis of the report**

- a. With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).
- b. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international search was carried out on the basis of the sequence listing:
- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

2. ☒ Certain claims were found unsearchable (See Box I).

3. ☐ Unity of invention is lacking (see Box II).

**4. With regard to the title,**

- ☒ the text is approved as submitted by the applicant.
- ☐ the text has been established by this Authority to read as follows:

**5. With regard to the abstract,**

- ☒ the text is approved as submitted by the applicant.
- ☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is Figure No.

- ☐ as suggested by the applicant.
- ☐ because the applicant failed to suggest a figure.
- ☐ because this figure better characterizes the invention.

☒ None of the figures.

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/GB 99/02833

## B x I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☒ Claims Nos.: 1-35 (all in part)  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## B x II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-35 (all in part)

Present claims 1-35 relate to an extremely large number of possible polymer types. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the polymers claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the polyarylether ketones or polyarylether sulphones described in the examples of the present application.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/02833

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G65/48 C08J5/22 H01M6/18 H01M10/40 H01M8/10  
H01M2/16

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C08G C08J H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 574 791 A (HOECHST AG) 22 December 1993 (1993-12-22) cited in the application claims 1-19 page 7, line 35 - line 45 ---	1-35
X	WO 96 29360 A (CLAUSS JOACHIM ;DECKERS GREGOR (DE); HOECHST AG (DE); WITTELER HEL) 26 September 1996 (1996-09-26) cited in the application claims 1-30 *Structure (III)* page 7 ---	1-35
X	EP 0 382 440 A (ICI PLC) 16 August 1990 (1990-08-16) claims 1,2 ---	1-7, 16, 19, 34, 35
	---	
	- / - -	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## ° Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*G\* document member of the same patent family

Date of the actual completion of the international search

3 December 1999

Date of mailing of the international search report

17. 01. 2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

O'Sullivan, T

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/02833

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 748 485 A (COMMISSARIAT ENERGIE ATOMIQUE) 14 November 1997 (1997-11-14) claim 1; example 1 page 16, line 1 - line 6 ---	1-3, 19-31
X	EP 0 008 895 A (ICI PLC) 19 March 1980 (1980-03-19) cited in the application claim 1 example 1 page 4, line 22 - line 30 ---	32,33
X	EP 0 211 693 A (UNION CARBIDE CORP) 25 February 1987 (1987-02-25) column 11 -column 14 ---	32-34
P,X	EP 0 932 213 A (SUMITOMO CHEMICAL CO) 28 July 1999 (1999-07-28) claims 1,3 -----	1-35

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 99/02833

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0574791 A	22-12-1993	CA 2098238 A JP 6093114 A US 5438082 A US 5741408 A US 5561202 A	14-12-1993 05-04-1994 01-08-1995 21-04-1998 01-10-1996
WO 9629360 A	26-09-1996	DE 19510026 A DE 19545642 A DE 19548423 A DE 19610303 A CA 2215911 A EP 0815160 A JP 11502249 T	26-09-1996 12-06-1997 26-06-1997 25-09-1997 26-09-1996 07-01-1998 23-02-1999
EP 0382440 A	16-08-1990	AU 4907490 A CA 2009323 A JP 3014841 A	16-08-1990 08-08-1990 23-01-1991
FR 2748485 A	14-11-1997	CA 2254086 A EP 0897407 A WO 9742253 A	13-11-1997 24-02-1999 13-11-1997
EP 0008895 A	19-03-1980	EP 0008894 A EP 0029633 A JP 1512209 C JP 55036296 A JP 63051174 B JP 1390886 C JP 55048222 A JP 61036781 B JP 1650209 C JP 3012094 B JP 62089730 A JP 1584173 C JP 59074128 A JP 62028169 B JP 1594860 C JP 2017571 B JP 61043630 A US 4273903 A US 4268650 A	19-03-1980 03-06-1981 09-08-1989 13-03-1980 13-10-1988 23-07-1987 05-04-1980 20-08-1986 30-03-1992 19-02-1991 24-04-1987 22-10-1990 26-04-1984 18-06-1987 27-12-1990 20-04-1990 03-03-1986 16-06-1981 19-05-1981
EP 0211693 A	25-02-1987	CA 1257740 A JP 62116628 A US 4774311 A	18-07-1989 28-05-1987 27-09-1988
EP 0932213 A	28-07-1999	NONE	



WPI

Patent  
Office

INVESTOR IN PEOPLE

TI - Electrolyte membranes for fuel cells - comprising polysulphone having sulphonic acid gps. introduced into aromatic rings

AB - J09245818 A new electrolyte membrane for fuel cells is of a specific polysulphone which has repeating units of formula (1) and sulphonic acid groups which are introduced into the aromatic rings of the repeating unit. The membrane has an ion-exchanging capacity of 1.6-3.2 meq/g-resin and a pressing resistant load of at least 80 kgf/cm<sup>2</sup>. The production of the new electrolyte membrane is also claimed, where (i) the aromatic rings of the repeating unit are sulphonated so as to introduce sulphonic acid groups; (ii) a solution of the resultant sulphonated polysulphone which has an ion-exchanging capacity of 1.6-3.2 meq/g-resin is applied to a support; and (iii) the coating is heated at 40-80 deg. C for at least 12 hours to obtain a membrane.

- USE - For polymer electrolyte membrane (PEM) fuel cells. The fuel cells are used as a power source for electric vehicles.

- ADVANTAGE - The new membrane has a higher ion-exchange capacity as compared with conventional membranes, e.g., Nafion ((RTM) Dupont Corp.) with 0.91 meq/g-resin.

- (Dwg.0/2)

PN - JP9245818 A 19970919 DW199808 H01M8/02 005pp

PR - JP19960069448 19960229

PA - (AISW ) AISIN AW CO LTD

- (EQUO-N) EQUOS RES KK

MC - A05-J06 A10-E12 A10-E12A A11-A02B A11-B05 A12-E06B A12-M05 A12-T04C L03-E04

- X16-C X16-C01 X16-C01C X16-E06A X21-A01F X21-B01A

DC - A85 L03 X16 X21

IC - B01D71/68 ;C08G75/23 ;C08J5/22 ;H01M8/02 ;H01M8/10

AN - 1998-079914 [08]

PAJ

TI - ELECTROLYTE FILM FOR FUEL CELL AND MANUFACTURE THEREOF

AB - PROBLEM TO BE SOLVED: To provide an electrolyte film with higher ion exchange capacity than Nafion and high mechanical strength in spite of higher ion exchange capacity than sulfonated polysulfone, and provide the manufacturing method thereof.

- SOLUTION: An aromatic ring of polysulfone having a repeating unit represented by the formula is sulfonated to introduce a sulfonic acid group into the aromatic ring, and a sulfonated polysulfone solution having an ion exchange capacity from more than 1.6 milliequivalent/g resin to 3.2 milliequivalent/g resin is obtained as a film forming solution, and the sulfonated polysulfone solution obtained is applied to a substrate to form a coating film, then the coating film is heated at 40-80 deg.C for 12 hours or longer to obtain an electrolyte film. The electrolyte film for a fuel cell has high ion exchange capacity mentioned above, and high mechanical strength of a fitting load pressure of 80kgf/cm<sup>2</sup> or higher, and high molding capability.

PN - JP9245818 A 19970919

PD - 1997-09-19

ABD - 19980130

ABV - 199801

AP - JP19960069448 19960229

PA - AISIN AW CO LTD;AQUEOUS RES:KK

IN - AZUMA RYUJI;NAGAI KENJI;KONDO MASAKO;MURASE KAZUHISA;TAKADA CHIKAYUKI

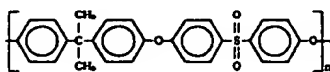
I - H01M8/02 ;B01D71/68 ;C08G75/23 ;C08J5/22 ;H01M8/10



The  
Patent  
Office



INVESTOR IN PEOPLE



<First Page Image>





Application No: GB 9921380.3  
Claims searched: 1-33, 35

Examiner: Martin Price  
Date of search: 7 December 1999

**Patents Act 1977**  
**Search Report under Section 17**

RECEIVED  
JUL 03 2000  
TC 1700

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:  
UK CI (Ed.Q): C3R - R36S; H1B - B300  
Int CI (Ed.6): C08G; H01M 8/10  
Other: Online - WPI, EPODOC, PAJ

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
X	GB 2316802 A (RFSUNY)	34
X,P	EP 0932213 A1 ( <del>Hoechst</del> ) (Sumitomo)	1-33,35
X	EP 0688824 A2 (Hoechst)	1-33,35
X	EP 0575807 A1 (Hoechst)	1-33,35
X	EP 0202850 (ICI)	1-33,35
X	EP 0182506 A2 (ICI)	1-33,35
X,P	WO 99/29763 (Aventis)	1-33,35
X	WO 96/29359 A1 (Hoechst)	1-33,35
X	US 5561202 (Hoechst)	1-33,35
X	US 5438082 (Hoechst)	1-33,35
X	US 5271813 (Florida)	1-33, 35
X	US 5112892 (ICI)	1-33, 35
X	WPI Accession number 1998-189383[17] & JP 10045913 (Sumitomo) - see abstract	1-33,35

X Document indicating lack of novelty or inventive step  
Y Document indicating lack of inventive step if combined with one or more other documents of same category.  
& Member of the same patent family

A Document indicating technological background and/or state of the art.  
P Document published on or after the declared priority date but before the filing date of this invention.  
E Patent document published on or after, but with priority date earlier than, the filing date of this application.



The  
Patent  
Office



INVESTOR IN PEOPLE

Application No: GB 9921380.3  
Claims searched: 1-33, 35

Examiner: Martin Price  
Date of search: 7 December 1999

Category	Identity of document and relevant passage	Relevant to claims
X	WPI Accession number 1998-079914[08] & JP 9245818 (Aisin) - see abstract	1-33,35

X Document indicating lack of novelty or inventive step  
Y Document indicating lack of inventive step if combined with one or more other documents of same category.  
& Member of the same patent family

A Document indicating technological background and/or state of the art.  
P Document published on or after the declared priority date but before the filing date of this invention.  
E Patent document published on or after, but with priority date earlier than, the filing date of this application.

1/PR+5

09/787011

JC08 Rec'd PCT/PTO 12 MAR 2001

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Larvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 99/02833

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G65/48 C08J5/22 H01M6/18 H01M10/40 H01M8/10  
H01M2/16

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C08J H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 574 791 A (HOECHST AG) 22 December 1993 (1993-12-22) cited in the application claims 1-19 page 7, line 35 - line 45 ---	1-35
X	WO 96 29360 A (CLAUSS JOACHIM ;DECKERS GREGOR (DE); HOECHST AG (DE); WITTELER HEL) 26 September 1996 (1996-09-26) cited in the application claims 1-30 *Structure (III)* page 7 ---	1-35
X	EP 0 382 440 A (ICI PLC) 16 August 1990 (1990-08-16) claims 1,2 ---	1-7, 16, 19, 34, 35
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

3 December 1999

Date of mailing of the international search report

17. 01. 2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

O'Sullivan, T

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 99/02833

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 748 485 A (COMMISSARIAT ENERGIE ATOMIQUE) 14 November 1997 (1997-11-14) claim 1; example 1 page 16, line 1 - line 6 ---	1-3, 19-31
X	EP 0 008 895 A (ICI PLC) 19 March 1980 (1980-03-19) cited in the application claim 1 example 1 page 4, line 22 - line 30 ---	32,33
X	EP 0 211 693 A (UNION CARBIDE CORP) 25 February 1987 (1987-02-25) column 11 -column 14 ---	32-34
P,X	EP 0 932 213 A (SUMITOMO CHEMICAL CO) 28 July 1999 (1999-07-28) claims 1,3 -----	1-35

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/GB 99/02833

### Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1-35 (all in part)  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

### Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

#### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/GB 99/02833

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-35 (all in part)

Present claims 1-35 relate to an extremely large number of possible polymer types. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the polymers claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the polyarylether ketones or polyarylether sulphones described in the examples of the present application.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PC1, JB 99/02833

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0574791 A	22-12-1993	CA 2098238 A	14-12-1993
		JP 6093114 A	05-04-1994
		US 5438082 A	01-08-1995
		US 5741408 A	21-04-1998
		US 5561202 A	01-10-1996
WO 9629360 A	26-09-1996	DE 19510026 A	26-09-1996
		DE 19545642 A	12-06-1997
		DE 19548423 A	26-06-1997
		DE 19610303 A	25-09-1997
		CA 2215911 A	26-09-1996
		EP 0815160 A	07-01-1998
		JP 11502249 T	23-02-1999
EP 0382440 A	16-08-1990	AU 4907490 A	16-08-1990
		CA 2009323 A	08-08-1990
		JP 3014841 A	23-01-1991
FR 2748485 A	14-11-1997	CA 2254086 A	13-11-1997
		EP 0897407 A	24-02-1999
		WO 9742253 A	13-11-1997
EP 0008895 A	19-03-1980	EP 0008894 A	19-03-1980
		EP 0029633 A	03-06-1981
		JP 1512209 C	09-08-1989
		JP 55036296 A	13-03-1980
		JP 63051174 B	13-10-1988
		JP 1390886 C	23-07-1987
		JP 55048222 A	05-04-1980
		JP 61036781 B	20-08-1986
		JP 1650209 C	30-03-1992
		JP 3012094 B	19-02-1991
		JP 62089730 A	24-04-1987
		JP 1584173 C	22-10-1990
		JP 59074128 A	26-04-1984
		JP 62028169 B	18-06-1987
		JP 1594860 C	27-12-1990
		JP 2017571 B	20-04-1990
		JP 61043630 A	03-03-1986
		US 4273903 A	16-06-1981
		US 4268650 A	19-05-1981
EP 0211693 A	25-02-1987	CA 1257740 A	18-07-1989
		JP 62116628 A	28-05-1987
		US 4774311 A	27-09-1988
EP 0932213 A	28-07-1999	NONE	





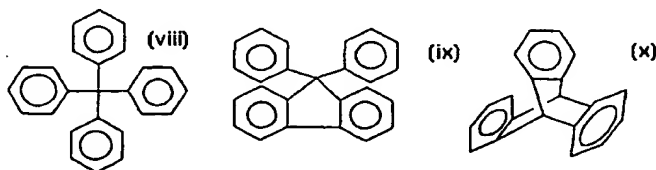
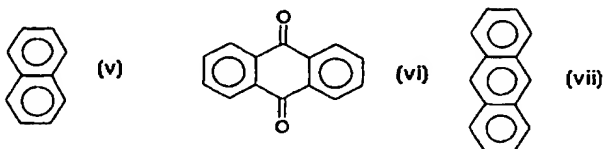
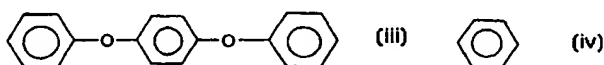
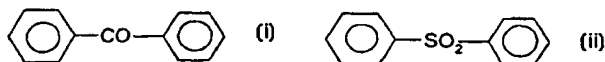
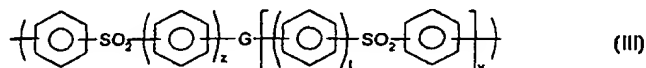
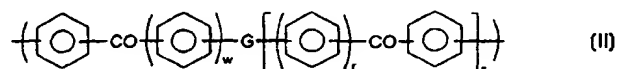
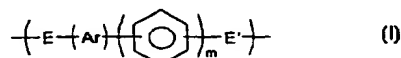
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>7</sup> : <b>C08G 65/48, C08J 5/22, H01M 6/18, 10/40, 8/10, 2/16</b>		<b>A1</b>	(11) International Publication Number: <b>WO 00/15691</b>
			(43) International Publication Date: 23 March 2000 (23.03.00)
(21) International Application Number: PCT/GB99/02833		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 10 September 1999 (10.09.99)		<b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(30) Priority Data:			
9819706.4                      11 September 1998 (11.09.98)    GB 9820940.6                      28 September 1998 (28.09.98)    GB 9913572.5                      11 June 1999 (11.06.99)            GB			
(71) Applicant (for all designated States except US): VICTREX MANUFACTURING LIMITED [GB/GB]; Victrex Technology Centre, Hillhouse International, P.O. Box 4, Thornton Cleveleys, Lancashire FY5 4QD (GB).			
(72) Inventors; and			
(75) Inventors/Applicants (for US only): CHARNOCK, Peter [GB/GB]; 7 Elvaston Road, Carleton, Poulton-Le-Fylde, Lancashire FY6 7TH (GB). KEMMISH, David, John [GB/GB]; 10 Whittle Green, Woodplumpton, Preston, Lancashire PR4 0WG (GB). STANILAND, Philip, Anthony [GB/GB]; 3 Foster Street, Broughton, Saltburn by the Sea, Cleveland TS12 2TR (GB). WILSON, Brian [GB/GB]; 1 White Lea, Cabus, Garstang, Lancashire PR3 1JG (GB).			
(74) Agents: BRIERLEY, Anthony, Paul et al.; Appleyard Lees, 15 Clare Road, Halifax HX1 2HY (GB).			

(54) Title: ION-EXCHANGE POLYMERS

## (57) Abstract

Ion-Exchange polymers for a polymer electrolyte membrane include a moiety of formula (I), and/or a moiety of formula (II), and/or a moiety of formula (III) wherein at least some of the units I, II and/or III are sulphonated; wherein the phenyl moieties in units I, II, and III are independently optionally substituted and optionally cross-linked; and wherein m, r, s, t, v, w and z independently represent zero or a positive integer, E and E' independently represent an oxygen or a sulphur atom or a direct link, G represents an oxygen or sulphur atom, a direct link or a -O-Ph-O- moiety where Ph represents a phenyl group and Ar is selected from one of the above moieties (i) to (x) which is bonded via one or more of its phenyl moieties to adjacent moieties.



**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

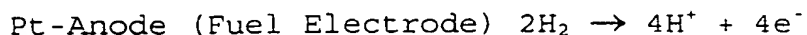
ION-EXCHANGE POLYMERS

This invention relates to ion-exchange polymers and particularly, although not exclusively, relates to  
5 sulphonated polymers, for example sulphonated polyaryletherketones, polyarylethersulphones and/or copolymers of the aforesaid. Preferred embodiments of the invention relate to ion-conductive membranes, for example of polymer electrolyte membrane fuel cells, made using such  
10 polymers. The invention also relates to novel non-sulphonated polyaryletherketones and/or polyarylethersulphones used for preparing said sulphonated polymers and processes for the preparation of polymers described herein.

15

A polymer electrolyte membrane fuel cell (PEMFC), shown schematically in Figure 1 of the accompanying diagrammatic drawings, may comprise a thin sheet 2 of a hydrogen-ion conducting Polymer Electrolyte Membrane (PEM) sandwiched on  
20 both sides by a layer 4 of platinum catalyst and an electrode 6. The layers 2, 4, 6 make up a Membrane Electrode Assembly (MEA) of less than 1mm thickness.

In a PEMFC, hydrogen is introduced at the anode (fuel  
25 electrode) which results in the following electrochemical reaction:



30 The hydrogen ions migrate through the conducting PEM to the cathode. Simultaneously, an oxidant is introduced at the cathode (oxidant electrode) where the following electrochemical reaction takes place:

Pt-Cathode (Oxidant Electrode)  $O_2 + 4H^+ = 4e^- \rightarrow 2H_2O$

Thus, electrons and protons are consumed to produce  
5 water and heat. Connecting the two electrodes through an  
external circuit causes an electrical current to flow in  
the circuit and withdraw electrical power from the cell.

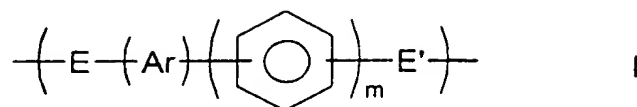
US Patent No. 5 561 202 (Hoechst) discloses the  
10 production of PEMs from sulphonated aromatic polyether  
ketones. At least 5% of the sulphonic groups in the  
sulphonic acid moieties are converted into sulphonyl  
chloride groups and then reacted with an amine containing  
at least one cross-linkable substituent or a further  
15 functional group. An aromatic sulphonamide is then  
isolated, dissolved in an organic solvent, converted into a  
film and then the cross-linkable substituents in the film  
are cross-linked. The invention is said to provide ion-  
conductive membranes suitable for use as polymeric solid  
20 electrolytes which have adequate chemical stability and can  
be produced from polymers which are soluble in suitable  
solvents.

One problem associated with known PEMFCs is that of  
25 providing PEMs which have desirable properties at elevated  
temperatures and which are cheap to manufacture.

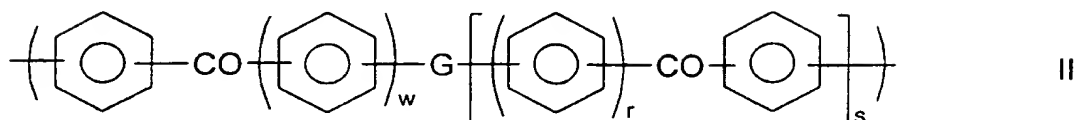
It is an object of the present invention to address  
problems associated with PEMs.

30

According to a first aspect of the invention, there is  
provided a polymer electrolyte membrane which includes a  
polymer having a moiety of formula

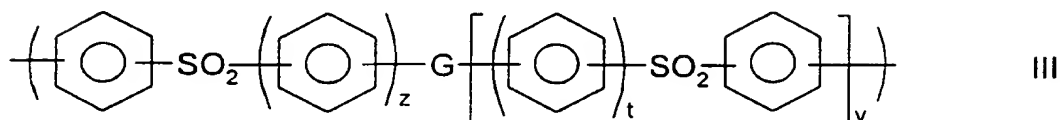


and/or a moiety of formula

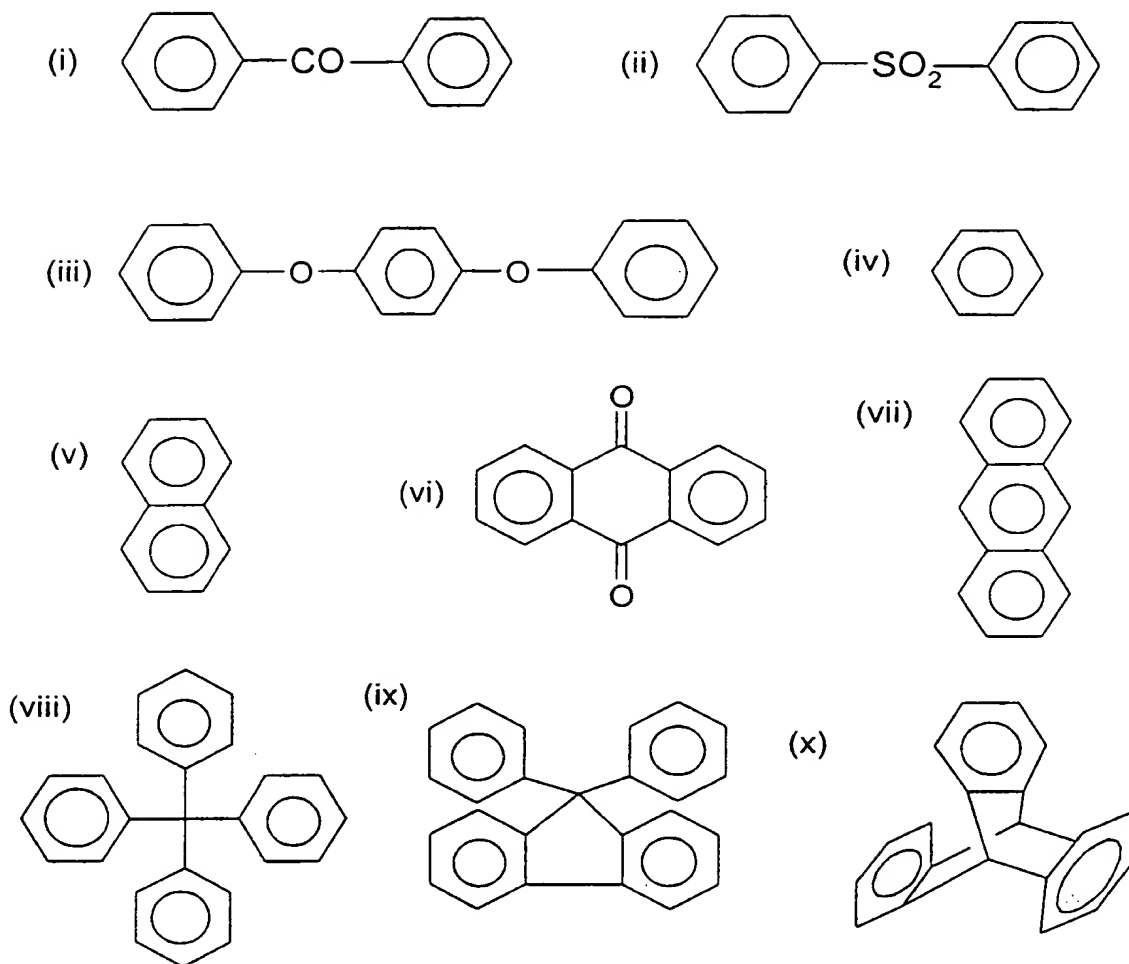


5

and/or a moiety of formula



wherein at least some of the units I, II and/or III are  
 10 sulphonated; wherein the phenyl moieties in units I, II,  
 and III are independently optionally substituted and  
 optionally cross-linked; and wherein m, r, s, t, v, w and z  
 independently represent zero or a positive integer, E and  
 E' independently represent an oxygen or a sulphur atom or a  
 15 direct link, G represents an oxygen or sulphur atom, a  
 direct link or a -O-Ph-O- moiety where Ph represents a  
 phenyl group and Ar is selected from one of the following  
 moieties (i) to (x) which is bonded via one or more of its  
 phenyl moieties to adjacent moieties



The invention extends to a polymer electrolyte membrane which includes a polymer having a moiety of formula I and/or a moiety of formula II and/or a moiety of formula III as described according to said first aspect, wherein at least some of units I, II and/or III are functionalised to provide ion exchange sites. Suitably, to provide said ion exchange sites, said polymer is sulphonated, phosphorylated, carboxylated, quaternary-aminoalkylated or chloromethylated, and optionally further modified to yield  $-\text{CH}_2\text{PO}_3\text{H}_2$ ,  $-\text{CH}_2\text{NR}_3^{20+}$  where  $\text{R}^{20}$  is an alkyl, or  $-\text{CH}_2\text{NAr}_3^{x+}$  where  $\text{Ar}^x$  is an aromatic (arene), to provide a cation or anion exchange membrane. Further still, the aromatic moiety may

contain a hydroxyl group which can be readily elaborated by existing methods to generate  $-\text{OSO}_3\text{H}$  and  $-\text{OPO}_3\text{H}_2$  cationic exchange sites on the polymer. Ion exchange sites of the type stated may be provided as described in WO95/08581.

5

References to sulphonation include a reference to substitution with a group  $-\text{SO}_3\text{M}$  wherein M stands for one or more elements selected with due consideration to ionic valencies from the following group: H,  $\text{NR}_4^{Y+}$ , in which  $\text{R}^Y$  stands for H,  $\text{C}_1\text{-C}_4$  alkyl, or an alkali or alkaline earth metal or a metal of sub-group 8, preferably H,  $\text{NR}_4^+$ , Na, K, Ca, Mg, Fe, and Pt. Preferably M represents H. Sulphonation of the type stated may be provided as described in WO96/29360.

15

Unless otherwise stated in this specification, a phenyl moiety may have 1,4- or 1,3-, especially 1,4-, linkages to moieties to which it is bonded.

20

Said polymer may include more than one different type of repeat unit of formula I; more than one different type of repeat unit of formula II; and more than one different type of repeat unit of formula III.

25

Said moieties I, II and III are suitably repeat units. In the polymer, units I, II and/or III are suitably bonded to one another - that is, with no other atoms or groups being bonded between units I, II, and III.

30

Where the phenyl moieties in units I, II or III are optionally substituted, they may be optionally substituted by one or more halogen, especially fluorine and chlorine, atoms or alkyl, cycloalkyl or phenyl groups. Preferred

alkyl groups are  $C_{1-10}$ , especially  $C_{1-4}$ , alkyl groups. Preferred cycloalkyl groups include cyclohexyl and multicyclic groups, for example adamantyl. In some cases, the optional substituents may be used in the cross-linking of the polymer. For example, hydrocarbon optional substituents may be functionalised, for example sulphonated, to allow a cross-linking reaction to take place. Preferably, said phenyl moieties are unsubstituted.

Another group of optional substituents of the phenyl moieties in units I, II or III include alkyls, halogens,  $C_yF_{2y+1}$  where  $y$  is an integer greater than zero,  $O-R^q$  (where  $R^q$  is selected from the group consisting of alkyls, perfluoralkyls and aryls),  $CF=CF_2$ ,  $CN$ ,  $NO_2$  and  $OH$ . Trifluormethylated phenyl moieties may be preferred in some circumstances.

Where said polymer is cross-linked, it is suitably cross-linked so as to improve its properties as a polymer electrolyte membrane, for example to reduce its swellability in water. Any suitable means may be used to effect cross-linking. For example, where  $E$  represents a sulphur atom, cross-linking between polymer chains may be effected via sulphur atoms on respective chains. Alternatively, said polymer may be cross-linked via sulphonamide bridges as described in US 5 561 202. A further alternative is to effect cross-linking as described in EP-A-0008895.

However, for polymers according to the first aspect or second aspect which are crystalline (which some are) there may be no need to effect cross-linking to produce a material which can be used as a polymer electrolyte



membrane. Such polymers may be easier to prepare than cross-linked polymers. Thus, said polymer of the first and/or second aspects may be crystalline. Preferably, said polymer is not optionally cross-linked as described.

5

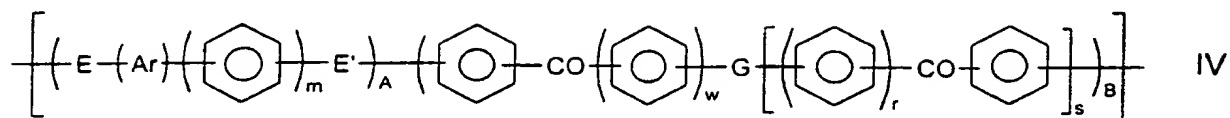
Where  $w$  and/or  $z$  is/are greater than zero, the respective phenylene moieties may independently have 1,4- or 1,3-linkages to the other moieties in the repeat units of formulae II and/or III. Preferably, said phenylene  
10 moieties have 1,4- linkages.

Preferably, the polymeric chain of the polymer does not include a -S- moiety. Preferably, G represents a direct link.

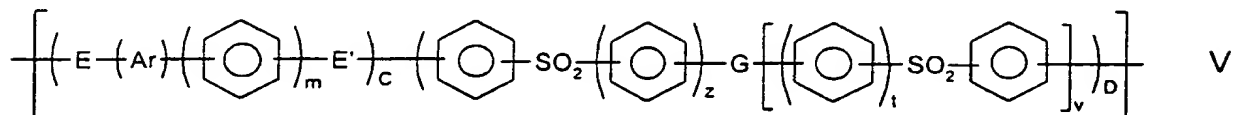
15

Suitably, "a" represents the mole % of units of formula I in said polymer, suitably wherein each unit I is the same; "b" represents the mole % of units of formula II in said polymer, suitably wherein each unit II is the same;  
20 and "c" represents the mole % of units of formula III in said polymer, suitably wherein each unit III is the same. Preferably, a is in the range 45-100, more preferably in the range 45-55, especially in the range 48-52. Preferably, the sum of b and c is in the range 0-55, more  
25 preferably in the range 45-55, especially in the range 48-52. Preferably, the ratio of a to the sum of b and c is in the range 0.9 to 1.1 and, more preferably, is about 1. Suitably, the sum of a, b and c is at least 90, preferably at least 95, more preferably at least 99, especially about  
30 100. Preferably, said polymer consists essentially of moieties I, II and/or III.

Said polymer may be a homopolymer having a repeat unit of general formula



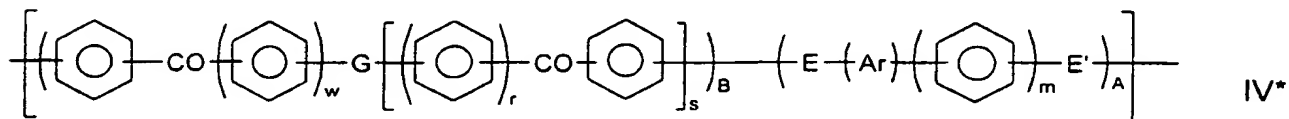
or a homopolymer having a repeat unit of general  
5 formula



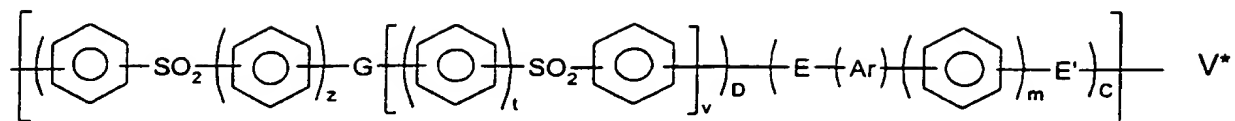
or a random or block copolymer of at least two different units of IV and/or V

10 wherein A, B, C and D independently represent 0 or 1 and E, E', G, Ar, m, r, s, t, v, w and z are as described in any statement herein.

As an alternative to a polymer comprising units IV  
15 and/or V discussed above, said polymer may be a homopolymer having a repeat unit of general formula



or a homopolymer having a repeat unit of general  
20 formula



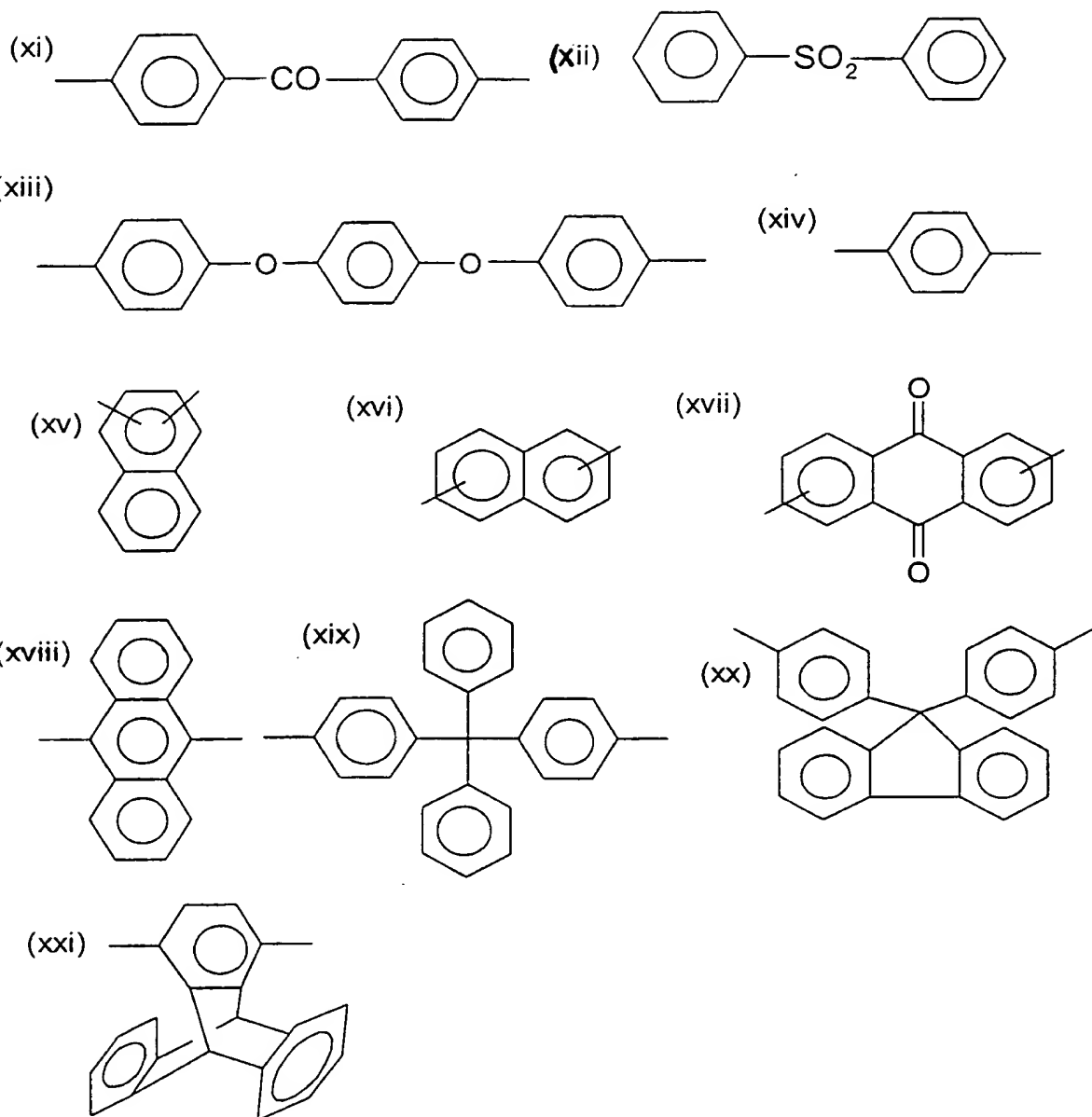
or a random or block copolymer of at least two different units of IV\* and/or V\*, wherein A, B, C, and D independently represent 0 or 1 and E, E', G, Ar, m, r, s, t, v, w and z are as described in any statement herein.

5

Preferably, m is in the range 0-3, more preferably 0-2, especially 0-1. Preferably, r is in the range 0-3, more preferably 0-2, especially 0-1. Preferably t is in the range 0-3, more preferably 0-2, especially 0-1.

10 Preferably, s is 0 or 1. Preferably v is 0 or 1. Preferably, w is 0 or 1. Preferably z is 0 or 1.

Preferably Ar is selected from the following moieties (xi) to (xxi):



Preferably, (xv) is selected from a 1,2-, 1,3-, or a 1,5-moiety; (xvi) is selected from a 1,6-, 2,3-, 2,6- or a 2,7-moiety; and (xvii) is selected from a 1,2-, 1,4-, 1,5-, 1,8- or a 2,6- moiety.

5

One preferred class of polymers may include at least some ketone moieties in the polymeric chain. In such a preferred class, the polymer preferably does not only include -O- and -SO<sub>2</sub>- moieties between aryl (or other  
10 unsaturated) moieties in the polymeric chain. Thus, in this case, suitably, a polymer of the first and/or second aspects does not consist only of moieties of formula III, but also includes moieties of formula I and/or II.

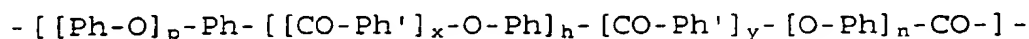
15 One preferred class of polymers does not include any moieties of formula III, but suitably only includes moieties of formulae I and/or II. Where said polymer is a homopolymer or random or block copolymer as described, said homopolymer or copolymer suitably includes a repeat unit of  
20 general formula IV. Such a polymer may, in some embodiments, not include any repeat unit of general formula V.

Referring to formula IV, preferably, said polymer is  
25 not a polymer wherein: Ar represents moiety (iv), E and E' represent oxygen atoms, m represents zero, w represents 1, s represents zero, and A and B represent 1; Ar represents moiety (i), E and E' represent oxygen atoms, G represents a direct link, m represents zero, w represents 1, r  
30 represents 0, s represents 1 and A and B represent 1; Ar represents moiety (iv), E and E' represent oxygen atoms, G represents a direct link, m represents 0, w represents 0, s represents 1, r represents 1 and A and B represent 1.

Referring to formula V, preferably Ar represents moiety (iv), E and E' represent oxygen atoms, G represents a direct link, m represents zero, z represents 1, v represents zero and C and D represent 1.

5

Preferably, said polymer is not a sulphonated aromatic polyetherketone of formula

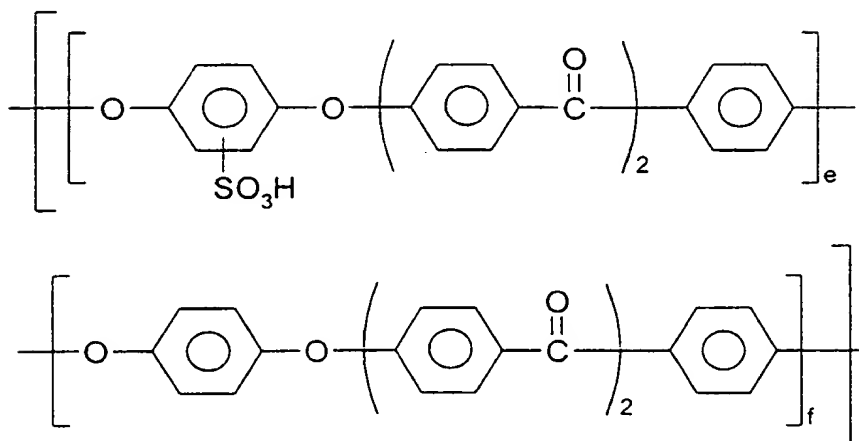


10

where Ph represents a 1,4- or 1,3- phenylene moiety; Ph' represents phenylene, naphthylene, biphenylene or anthrylene; p is 1, 2, 3 or 4; x, h and n are, independently, zero or 1; and y is 1, 2 or 3.

15

Preferably, said polymer does not conform to the formula



20

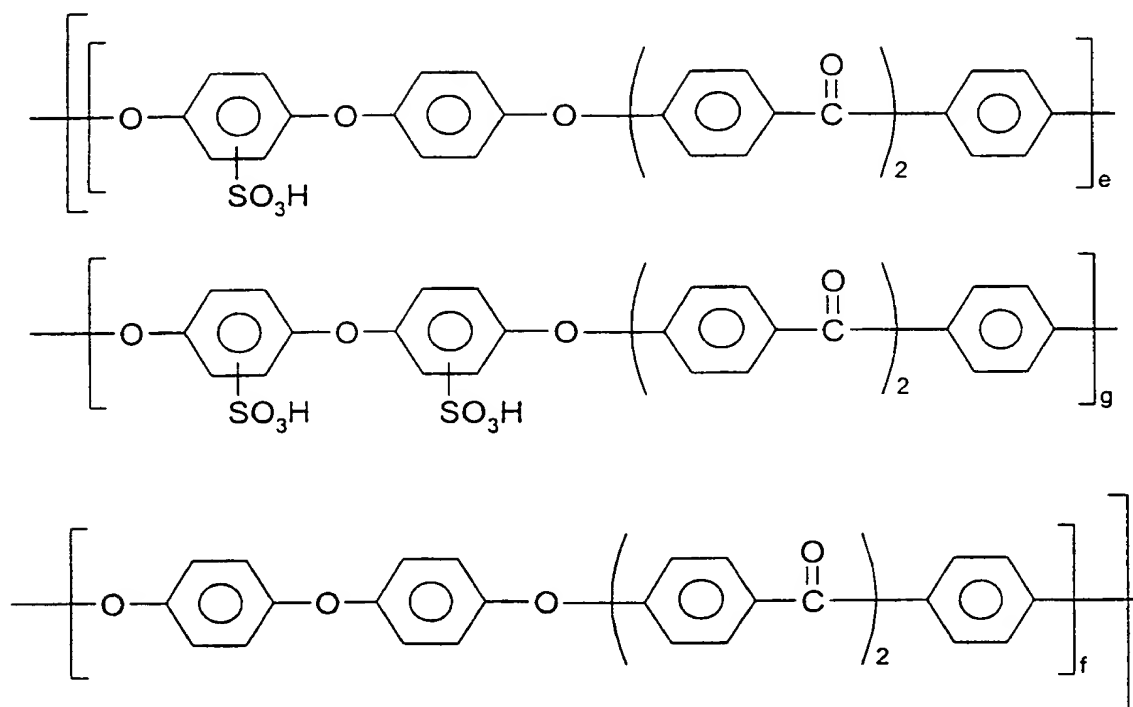
where

e is from 0.2 to 1,

f is from 0 to 0.8, and

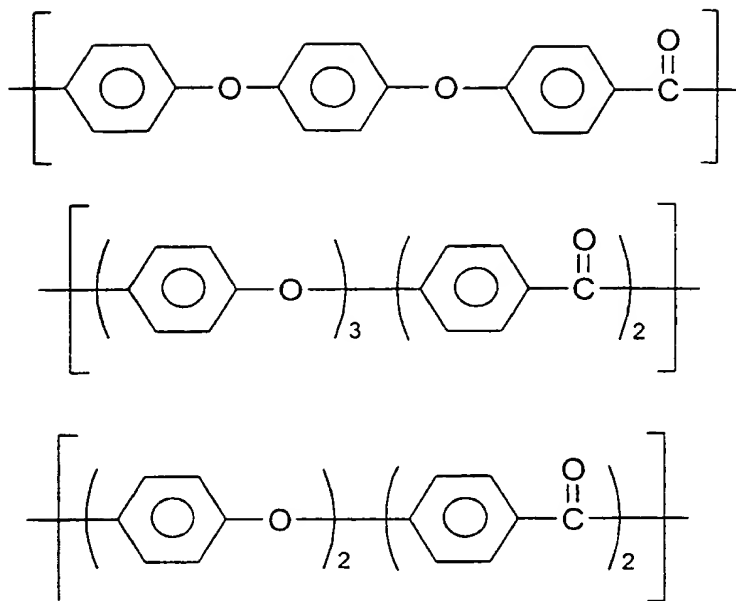
e + f = 1

Preferably, said polymer does not conform to the formula



5 in which e is a number from 0 to 1, g is a number from 0 to 1, f is a number from 0 to 0.5, and the sum  $e + f + g = 1$ .

Preferably, said polymer is not a copolymer built up  
 10 from at least two different units of formulae:



Suitable moieties Ar are moieties (i), (ii), (iv) and (v) and, of these, moieties (i), (ii) and (iv) are preferred. Preferred moieties Ar are moieties (xi), (xii), (xiv), (xv) and (xvi) and, of these, moieties (xi), (xii) and (xiv) are especially preferred. Another preferred moiety is moiety (v), especially, moiety (xvi). In relation, in particular to the alternative polymers comprising units IV\* and/or V\*, preferred Ar moieties are (v) and, especially, (xvi).

Preferred polymers include an electron-rich, relatively non-deactivated, easily sulphonatable unit, for example a multi-phenylene moiety or a fused-rings aromatic moiety, such as naphthalene. Such an easy to sulphonate unit may be sulphonated under relatively mild conditions to introduce two sulphonate groups per unit. Thus, preferred polymers may have at least  $10\pi$  electrons in a delocalized aromatic moiety. The number of  $\pi$  electrons may be 12 or less.



Preferred polymers include a biphenylene moiety. Other preferred polymers include a naphthalene moiety. Preferred polymers include said electron rich, non-deactivated, easily sulphonatable unit bonded to two oxygen atoms.  
5 Especially preferred polymers include a -O-biphenylene-O-moiety. Other especially preferred polymers include a -O-naphthalene-O- moiety.

Preferred polymers include a first type of moiety which  
10 is relatively difficult to sulphonate and a second type of moiety which is relatively easy to sulphonate. For example, said second moiety may be sulphonatable using the relatively mild method described in Example 13 hereinafter, whereas the first moiety may be substantially non-  
15 sulphonatable in such a method. The use of the method of Example 13 may be advantageous over currently used methods which use oleum. A preferred second said moiety includes a moiety  $-\text{Ph}_n-$  wherein  $n$  is an integer of at least 2. Said moiety is preferably bound to at least one ether oxygen.  
20 Especially preferred is the case wherein said moiety is  $-\text{O}-\text{Ph}_n-\text{O}-$  where said ether groups are para to the Ph-Ph bond.

Preferred polymers are copolymers comprising a first repeat unit which is selected from the following:

25

(a) a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv),  $m$  and  $s$  represent zero,  $w$  represents 1 and A and B represent 1;

30

(b) a unit of formula IV wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety

of structure (i), m represents zero, A represents 1, B represents zero;

(c) a unit of formula V wherein E and E' represent  
5 oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and v represent zero, z represents 1 and C and D represent 1;

(d) a unit of formula V wherein E represents an oxygen  
10 atom, E' represents a direct link, Ar represents a moiety of structure (ii), m represents 0, C represents 1, D represents 0; or

(e) a unit of formula V wherein E and E' represents an  
15 oxygen atom, Ar represents a structure (i), m represents 0, C represents 1, Z represents 1, G represents a direct link, v represents 0 and D represents 1;

and a second repeat unit which is selected from the  
20 following:

(f) a unit of formula IV wherein E and E' represent  
oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, w represents 1, s  
25 represents zero, A and B represent 1;

(g) a unit of formula IV wherein E represents an oxygen  
atom, E' is a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent  
30 zero, w represent 1, A and B represent 1;

(h) a unit of formula V wherein E and E' represent  
oxygen atoms, G represents a direct link, Ar represents a

moiety of structure (iv), m represents 1, z represents 1, v represents 0, C and D represent 1; and

(i) a unit of formula V wherein E represents an oxygen atom, E' represents a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and v represent zero, z represents 1, C and D represent 1;

Other second units which may form copolymers with any of said first repeat units (a) to (e) above include: a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (v), m represents 0, w represents 1, s represents 0, A and B represent 1; or a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (v), m represents 0, z represents 1, v represents 0, **C** and **D** represent 1.

Preferred polymers for some situations may comprise first units selected from (a), (b), (c) and (e) and second units selected from (f), (g), (h) or (i). A polymer comprising units (d) and (h) may also be preferred.

More preferred polymers are copolymers having a first repeat unit selected from those described above, especially repeat units (b), (d) or (e) in combination with a second repeat unit selected from units (f) or (h).

Preferred polymers having repeat unit(s) of formulae IV\* and V\* may include: a unit of formula IV\* wherein Ar represents a moiety of structure (v), E represents a direct link, E' represents an oxygen atom, G represents a direct link, w, s and m represent 0, A and B represent 1; and/or a

repeat unit of formula V\* wherein Ar represents a moiety of structure (v), E represents a direct link, E' represents an oxygen atom, G represents a direct link, z, v and m represent 0, C and D represent 1.

5

Said polymers having repeat units IV\* and V\* may include any of repeat units (a) to (i) described above.

In some situations, polymers which include at least one repeat unit of formula IV or formula IV\* may be preferred.

Copolymers may be prepared having one or more first repeat units and one or more of said second repeat units.

Where said polymer is a copolymer as described, the mole% of co-monomer units, for example said first and second repeat units described above, may be varied to vary the solubility of the polymer in solvents, for example in organic solvents which may be used in the preparation of films and/or membranes from the polymers and/or in other solvents, especially water.

Preferred polymers suitably have a solubility of at least 10% w/v, preferably a solubility in the range 10 to 30 %w/v in a polar aprotic solvent, for example NMP, DMSO or DMF. Preferred polymers are substantially insoluble in boiling water.

First units of the type described above (with the exception of units (a) and (c)) may be relatively difficult to sulphonate, whereas second units of the type described may be easier to sulphonate.

Where a phenyl moiety is sulphonated, it may only be mono-sulphonated. However, in some situations it may be possible to effect bi- or multi-sulphonation.

5 In general terms, where a said polymer includes a -O-phenyl-O- moiety, up to 100 mole% of the phenyl moieties may be sulphonated. Where a said polymer includes a -O-biphenylene-O- moiety, up to 100 mole% of the phenyl moieties may be sulphonated. It is believed to be possible  
10 to sulphonate relatively easily -O-(phenyl)<sub>n</sub>-O- moieties wherein n is an integer, suitably 1-3, at up to 100 mole%. Moieties of formula -O-(phenyl)<sub>n</sub>-CO- or -O-(phenyl)<sub>n</sub>-SO<sub>2</sub>- may also be sulphonated at up to 100 mole% but more vigorous conditions may be required. Moieties of formulae  
15 -CO-(phenyl)<sub>n</sub>-CO- and -SO<sub>2</sub>-(phenyl)<sub>n</sub>-SO<sub>2</sub>- are more difficult to sulphonate and may be sulphonated to a level less than 100 mole% or not at all under some sulphonation conditions.

The glass transition temperature (T<sub>g</sub>) of said polymer  
20 may be at least 144°C, suitably at least 150°C, preferably at least 154°C, more preferably at least 160°C, especially at least 164°C. In some cases, the T<sub>g</sub> may be at least 170°C, or at least 190°C or greater than 250°C or even 300°C.

25

Said polymer may have an inherent viscosity (IV) of at least 0.1, suitably at least 0.3, preferably at least 0.4, more preferably at least 0.6, especially at least 0.7 (which corresponds to a reduced viscosity (RV) of least  
30 0.8) wherein RV is measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84gcm<sup>-3</sup>, said solution containing 1g of polymer per 100cm<sup>-3</sup> of solution. IV is measured at 25°C on a solution of polymer

in concentrated sulphuric acid of density  $1.84\text{gcm}^3$ , said solution containing  $0.1\text{g}$  of polymer per  $100\text{cm}^3$  of solution.

The measurements of both RV and IV both suitably employ  
5 a viscometer having a solvent flow time of approximately 2 minutes.

The main peak of the melting endotherm ( $T_m$ ) for said polymer (if crystalline) may be at least  $300^\circ\text{C}$ .

10

In general terms, said polymer is preferably substantially stable when used as a PEM in a fuel cell. Thus, it suitably has high resistance to oxidation, reduction and hydrolysis and has very low permeability to  
15 reactants in the fuel cell. Preferably, however, it has a high proton conductivity. Furthermore, it suitably has high mechanical strength and is capable of being bonded to other components which make up a membrane electrode assembly.

20

Said polymer may comprise a film, suitably having a thickness of less than  $1\text{mm}$ , preferably less than  $0.5\text{mm}$ , more preferably less than  $0.1\text{mm}$ , especially less than  $0.05\text{mm}$ . The film may have a thickness of at least  $5\mu\text{m}$ .

25

Said polymer electrolyte membrane may comprise one or more layers wherein, suitably, at least one layer comprises a film of said polymer. Said membrane may have a thickness of at least  $5\mu\text{m}$  and, suitably, less than  $1\text{mm}$ , preferably  
30 less than  $0.5\text{mm}$ , more preferably less than  $0.1\text{mm}$ , especially less than  $0.05\text{mm}$ .

The polymer electrolyte membrane may be a composite membrane which suitably includes a support material for the conductive polymer for importing mechanical strength and dimensional stability to the membrane. The polymer may be associated with the support material to form a composite membrane in a variety of ways. For example, an unsupported conductive polymer film can be preformed and laminated to the support material. Alternatively, (and preferably) the support material may be porous and a solution of the conductive polymer can be impregnated into the support material. In one embodiment, the support material may comprise, or preferably consist essentially of, polytetrafluoroethylene, suitably provided as a porous film. Such a support material may be as described and used in accordance with the teachings of WO97/25369 and WO96/28242, the contents of which are incorporated herein by reference. Suitably, the support material has a porous microstructure of polymeric fibrils and is impregnated with said polymer throughout the material, preferably so as to render an interior volume of the membrane substantially occlusive.

The use of support material as described may allow polymers of lower equivalent weights (EW) (for example less than 500 g/mol, less than 450 g/mol or even less than 400 g/mol or 370 g/mol) or relatively inflexible and/or brittle polymers to be used in polymer electrolyte membranes.

The polymer electrolyte membrane suitably includes a layer of a catalyst material, which may be a platinum catalyst (i.e. platinum containing) or a mixture of platinum and ruthenium, on both sides of the polymer film. Electrodes may be provided outside the catalyst material.

It may be preferable for each phenyl group in a sulphonated polymer as described to be deactivated by being bonded directly to an electron withdrawing group, for example a sulphonated group, a sulphone group or a ketone group.

According to a second aspect of the invention, there is provided a polymer electrolyte membrane which includes a polymer which includes: polyaryletherketone and/or polyarylethersulphone units; and units of formula  $-O-Ph_n-O-$  (XX) wherein Ph represents a phenyl group and n represents an integer of 2 or greater and wherein Ph groups of units (XX) are sulphonated.

Preferably, each phenyl group of moiety  $Ph_n$  is sulphonated, preferably mono-sulphonated. About 100 mole% of such phenyl groups may be sulphonated as described.

Preferably,  $-OPhCO-$  and/or  $-OPhSO_2-$  moieties of said polymer are sulphonated to a lesser extent than the phenyl groups of moiety  $Ph_n$ . Moieties  $-OPhCO-$  and  $-OPhSO_2-$  may be substantially non-sulphonated.

In one embodiment, said polymer may include no ketone linkages and may have an equivalent weight of more than 900. Nonetheless, it has been found, surprisingly, that such polymers are still conducting.

Said polymer electrolyte membrane may be for a fuel cell or an electrolyser.



The invention extends to the use of a polymer which includes relatively easy to sulphonate units and relatively difficult to sulphonate units in the preparation of a polymer for a polymer electrolyte membrane.

5

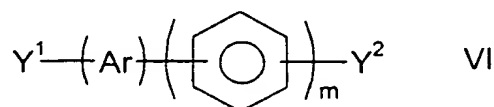
The polymer electrolyte membrane described herein may include a blend of polymers, at least one of which is a polymer described according to the invention described herein. Suitably the polymers described herein are blended with 0-40wt%, preferably 0-20wt%, more preferably 0-10wt%, especially 0-5wt% of other polymeric material. Preferably, however, a blend of polymers is not provided.

According to a third aspect of the invention, there is provided a fuel cell or an electrolyser (especially a fuel cell) incorporating a polymer electrolyte membrane according to the first or second aspects.

According to a fourth aspect of the invention, there is provided any novel polymer as described according to said first aspect per se.

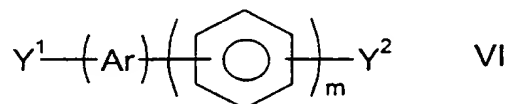
According to a fifth aspect of the invention, there is provided a process for the preparation of a polymer as described in the first, second, third and/or fourth aspects, the process comprising:

(a) polycondensing a compound of general formula

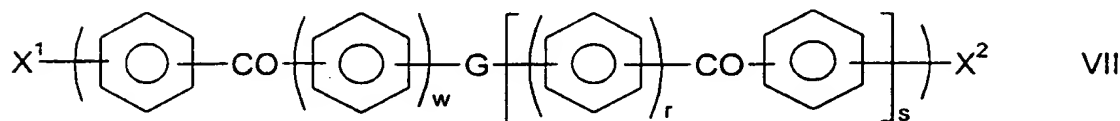


with itself wherein  $Y^1$  represents a halogen atom or a group  $-EH$  and  $Y^2$  represents a halogen atom or, if  $Y^1$  represents a halogen atom,  $Y^2$  represents a group  $E'H$ ; or

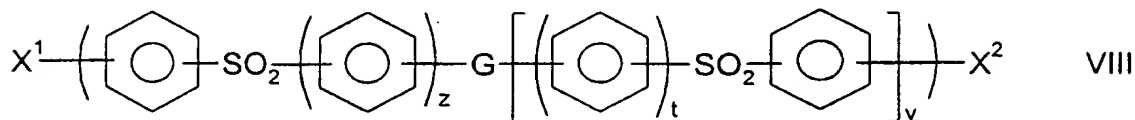
5 (b) polycondensing a compound of general formula



10 with a compound of formula



and/or with a compound of formula



15

wherein  $Y^1$  represents a halogen atom or a group  $-EH$  (or  $-E'H$  if appropriate) and  $X^1$  represents the other one of a halogen atom or group  $-EH$  (or  $-E'H$  if appropriate) and  $Y^2$  represents a halogen atom or a group  $-E'H$  and  $X^2$  represents the other one of a halogen atom or a group  $-E'H$  (or  $-EH$  if appropriate).

20

(c) optionally copolymerizing a product of a process as described in paragraph (a) with a product of a process as described in paragraph (b);

5 wherein the phenyl moieties of units VI, VII and/or VIII are optionally substituted; the compounds VI, VII and/or VIII are optionally sulphonated; and Ar, m, w, r, s, z, t, v, G, E and E' are as described above except that E and E' do not represent a direct link;

10 the process also optionally comprising sulphonating and/or cross-linking a product of the reaction described in paragraphs (a), (b) and/or (c) to prepare said polymer.

15 In some situations, the polymer prepared, more particularly phenyl groups thereof, may be optionally substituted with the groups hereinabove described after polymer formation.

20 Preferably, where  $Y^1$ ,  $Y^2$ ,  $X^1$  and/or  $X^2$  represent a halogen, especially a fluorine, atom, an activating group, especially a carbonyl or sulphone group, is arranged ortho- or para- to the halogen atom.

25 Advantageously, where it is desired to prepare a copolymer comprising a first repeat unit IV or V wherein E represent an oxygen or sulphur atom, Ar represents a moiety of structure (i), m represents zero, E' represents a direct link, A represents 1 and B represents zero and a second  
30 repeat unit IV or V wherein E and E' represent an oxygen or sulphur atom, Ar represents a moiety of structure (iv), m and w represent 1, G represents a direct link, s represents zero and A and B represent 1 wherein the polymer is not a

random polymer but has a regular structure, the process described in paragraph (b) above may be used wherein in said compound of general formula VI,  $Y^1$  and  $Y^2$  represent -OH or -SH groups, Ar represents a moiety of structure (iv) and m represents 1 and in said compounds of general formulae VII and VIII,  $X^1$  and  $X^2$  represent a fluorine atom, w,r,s,z,t and v represent 1 and G represents an oxygen or sulphur atom.

10 In another embodiment, where it is desired to prepare a copolymer comprising a first repeat unit IV or V wherein E and E' represent an oxygen or sulphur atom, Ar represents a moiety of structure (iv), m represents zero, A represents 1, w represents 1, s represents zero and B represents 1 and  
15 a second repeat unit IV or V wherein E and E' represent an oxygen or sulphur atom, Ar represents a moiety of structure (iv), m and w represent 1, s represents zero and A and B represent 1, wherein the polymer is not a random polymer but has a regular structure, the process described in  
20 paragraph (b) above may be used wherein in said compound of general formula VI,  $Y^1$  and  $Y^2$  represent -OH or -SH groups, Ar represents a moiety of structure (iv) and m represents 1 and in said compounds of general formulae VII and VIII,  $X^1$  and  $X^2$  represent a fluorine atom, w,r,s,z,t and v represent  
25 1 and G represents a -O-Ph-O- moiety.

Preferred halogen atoms are fluorine and chlorine atoms, with fluorine atoms being especially preferred. Preferably, halogen atoms are arranged meta- or para- to  
30 activating groups, especially carbonyl groups.

Where the process described in paragraph (a) is carried out, preferably one of  $Y^1$  and  $Y^2$  represents a fluorine atom

and the other represents an hydroxy group. More preferably in this case,  $Y^1$  represents a fluorine atom and  $Y^2$  represents an hydroxy group. Advantageously, the process described in paragraph (a) may be used when Ar represents a moiety of structure (i) and m represents 1.

When a process described in paragraph (b) is carried out, preferably,  $Y^1$  and  $Y^2$  each represent an hydroxy group. Preferably,  $X^1$  and  $X^2$  each represent a halogen atom, suitably the same halogen atom.

Compounds of general formula VI, VII and VIII are commercially available (eg from Aldrich U.K.) and/or may be prepared by standard techniques, generally involving Friedel-Crafts reactions, followed by appropriate derivatisation of functional groups. The preparations of some of the monomers described herein are described in P M Hergenrother, B J Jensen and S J Havens, Polymer 29, 358 (1988), H R Kricheldorf and U Delius, Macromolecules 22, 517 (1989) and P A Staniland, Bull, Soc, Chem, Belg., 98 (9-10), 667 (1989).

Where compounds VI, VII and/or VIII are sulphonated, compounds of formulas VI, VII and/or VIII which are not sulphonated may be prepared and such compounds may be sulphonated prior to said polycondensation reaction.

Sulphonation as described herein may be carried out in concentrated sulphuric acid (suitably at least 96% w/w, preferably at least 97%w/w, more preferably at least 98%w/w; and preferably less than 98.5%w/w) at an elevated temperature. For example, dried polymer may be contacted with sulphuric acid and heated with stirring at a

temperature of greater than 40°C, preferably greater than 55°C, for at least one hour, preferably at least two hours, more preferably about three hours. The desired product may be caused to precipitate, suitably by contact with cooled  
5 water, and isolated by standard techniques. Sulphonation may also be effected as described in US5362836 and/or EP0041780.

Where the process described in paragraph (b) is carried  
10 out, suitably, "a\*" represents the mole% of compound VI used in the process; "b\*" represents the mole % of compound VII used in the process; and "c\*" represents the mole % of compound VIII used in the process.

15 Preferably, a\* is in the range 45-55, especially in the range 48-52. Preferably, the sum of b\* and c\* is in the range 45-55, especially in the range 48-52. Preferably, the sum of a\*, b\* and c\* is 100.

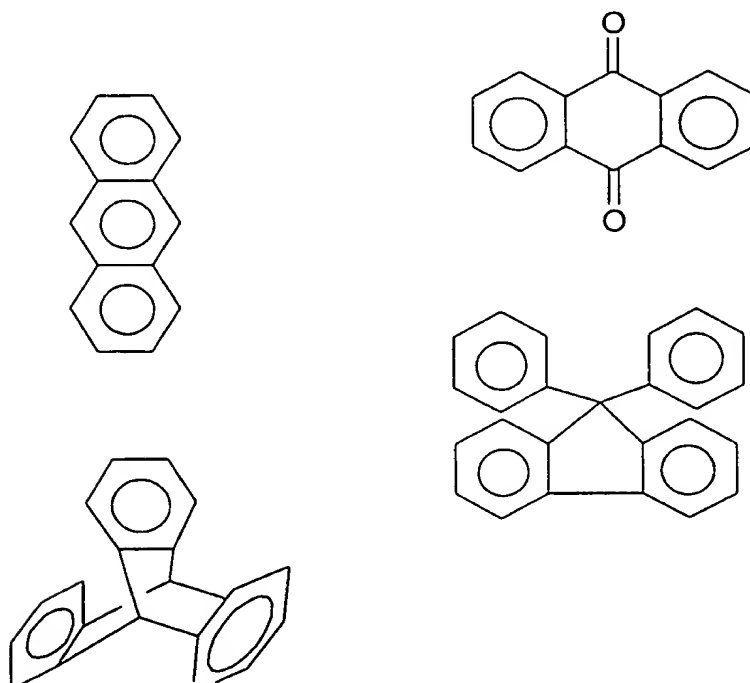
20 Where the process described in paragraph (b) is carried out, preferably, one of either the total mole % of halogen atoms or groups -EH/-E'H in compounds VI, VII and VIII is greater, for example by up to 10%, especially up to 5%, than the total mole % of the other one of either the total  
25 mole % of halogen atoms or groups -EH/-E'H in compounds VI, VII and VIII. Where the mole % of halogen atoms is greater, the polymer may have halogen end groups and be more stable than when the mole % of groups -EH/-E'H is greater in which case the polymer will have -EH/-E'H end groups. However,  
30 polymers having -EH/-E'H end groups may be advantageously cross-linked.

The molecular weight of the polymer can also be controlled by using an excess of halogen or hydroxy reactants. The excess may typically be in the range 0.1 to 5.0 mole %. The polymerisation reaction may be terminated  
5 by addition of one or more monofunctional reactants as end-cappers.

It is believed that certain polymers described herein are novel and, therefore, in a sixth aspect, the invention  
10 extends to any novel polymer described herein per se.

It is also believed that certain polymers according to said first and/or second aspect but which are not sulphonated are novel. Thus, according to a seventh aspect  
15 of the invention, there is provided a novel polymer having a moiety of formula I and/or a moiety of formula II and/or a moiety of formula III wherein E, E', G, m, r, s, t, v, w, z and Ar are as described in any statement herein.

20 Preferably, said polymer includes a moiety of formula II and/or III and Ar is selected from



Preferably, in the aforementioned formulae, each -Ar- is bonded to adjacent moieties as described in any statement herein.

5

According to an eighth aspect of the invention, there is provided a process for the preparation of novel polymers according to said seventh aspect, the process being as described according to the process of the fifth aspect except that compounds VI, VII and VIII are not sulphonated and the process does not include a sulphonation step.

Sulphonated polymers described herein may be made into films and/or membranes for use as PEMs by conventional techniques, for example as described in Examples 5 to 7 of US 5561202.

The sulphonated polymers described herein may be used as polymer electrolyte membranes in fuel cells or electrolysers as described. Additionally, they may be used in gas diffusion electrodes.

Any feature of any aspect of any invention or example described herein may be combined with any feature of any aspect of any other invention or example described herein.

Specific embodiments of the invention will now be described, by way of example, with reference to figure 1 which is a schematic representation of a polymer electrolyte membrane fuel cell.

30

As described above, the fuel cell includes a thin sheet of a hydrogen-ion conducting Polymer Electrolyte

2



Membrane. The preparation of sheet material for such a membrane is described hereinafter.

#### Example 1

5

A 700ml flanged flask fitted with a ground glass Quickfit lid, stirrer/stirrer guide, nitrogen inlet and outlet was charged with 4,4'-difluorobenzophenone (89.03g, 0.408 mole), 4,4'-dihydroxybenzophenone (34.28g, 0.16 mole), 4,4'-dihydroxybiphenyl (44.69g, 0.24 mole) and diphenylsulphone (332g) and purged with nitrogen for at least 1 hour. The contents were then heated under a nitrogen blanket to between 140 and 145°C to form an almost colourless solution. While maintaining a nitrogen blanket, dried sodium carbonate (43.24g, 0.408 mole) was added. The temperature was raised gradually to 335°C over 200 minutes then maintained for 1 hour.

The reaction mixture was allowed to cool, milled and washed with acetone and water. The resulting polymer was dried in an air oven at 120°C. The polymer had a Tg of 164°C, a melt viscosity at 400°C, 1000sec<sup>-1</sup> of 0.48 kNsm<sup>-2</sup> and an inherent viscosity (IV) 0.40 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84g.cm<sup>-3</sup>, said solution containing 0.1g of polymer/100cm<sup>3</sup>).

#### Examples 2 to 6

30

The polymerisation procedure of Example 1 was followed, except that copolymers of different compositions were prepared by varying the mole ratios of 4,4'-dihydroxybenzophenone to 4,4'-dihydroxybiphenyl, with the

sum of the number of moles of the aforesaid reactants equalling the number of moles of 4,4'-difluorobenzophenone, as described in Example 1. A summary of the mole ratios and the MV are detailed in the

5 table below.

Example No	4,4' dihydroxybiphenyl: 4,4' - dihydroxybenzophenone	MV (kNsm <sup>-2</sup> )
2	2:1	0.17
3a	1:1	0.48
3b*	1:1	0.69
4	1:2	0.54
5	1:3	0.43
6	1.25:1	0.34

\* The polymerisation procedure of Example 1 was followed except dried sodium carbonate (43.24g, 0.408 mole) was replaced by dried sodium carbonate (42.44g, 0.4 mole) and dried potassium carbonate (1.11g, 0.008 mole).

#### Example 7a

10 A 700ml flanged flask fitted with a ground glass Quickfit lid, stirrer/stirrer guide, nitrogen inlet and outlet was charged with 4,4'-difluorobenzophenone (89.03g, 0.408 mole), 4,4'-dihydroxybiphenyl (37.24g, 0.2 mole) 4,4'-dihydroxydiphenylsulphone (50.05g, 0.2 mole), and  
15 diphenylsulphone (332g) and purged with nitrogen for over 1 hour. The contents were then heated under a nitrogen blanket to between 140 and 150°C to form an almost colourless solution. While maintaining a nitrogen blanket, dried sodium carbonate (42.44g, 0.4 mole) and  
20 potassium carbonate (1.11g, 0.008 mole) were added. The temperature was raised gradually to 315°C over 3 hours then maintained for 0.5 hours.

The reaction mixture was allowed to cool, milled and washed with acetone and water. The resulting polymer was dried in an air oven at 120°C. The polymer had a Tg of 183°C, a melt viscosity at 400°C, 1000sec<sup>-1</sup> of 0.78 kNsm<sup>-2</sup> and an inherent viscosity (IV) 0.40 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84g.cm<sup>-3</sup>, the solution containing 0.1g of polymer/100cm<sup>3</sup>).

Example 7b

The polymerisation procedure of Example 7a was followed except dried sodium carbonate (42.44g, 0.4 mole) and dried potassium carbonate (1.11g, 0.008 mole) was replaced by dried sodium carbonate only (43.24g, 0.408 mole). The polymer had a Tg of 183°C and a melt viscosity at 400°C, 1000sec<sup>-1</sup> of 0.43 kNsm<sup>-2</sup>

Examples 8 and 10

The polymerisation procedure of Example 7b was followed, except that copolymers were prepared by varying the mole ratios of the hydroxy-containing reactants, with the sum of the number of moles of the aforesaid equalling the number of moles of 4,4'-difluorobenzophenone. A summary of the mole ratios and the MV are detailed in the table below.

Example No	4,4'-dihydroxybiphenyl : 4,4'-dihydroxydiphenyl-sulphone	MV(kNsm <sup>-2</sup> )
8	1:2	0.67
9	1:3	0.72
10	1:1.5	0.6

Example 11

A 700ml flanged flask fitted with a ground glass Quickfit lid, stirrer/stirrer guide, nitrogen inlet and outlet was charged with 4,4'-dichlorodiphenylsulphone (104.25g, 0.36 mole), 4,4'-dihydroxydiphenylsulphone (6.75g, 0.27 mole), 4,4'-dihydroxybiphenyl (16.74g, 0.09 mole) and diphenylsulphone (245g) and purged with nitrogen for at least 1 hour. The contents were then heated under a nitrogen blanket to between 140 and 145°C to form an almost colourless solution. While maintaining a nitrogen blanket potassium carbonates (50.76g, 0.37 mole) was added. The temperature was raised to 180°C, held for 0.5 hours, raised to 205°C, held for 1 hour, raised to 225°C, held for 2 hours, raised to 265°C, held for 0.5 hours, raised to 280°C and held for 2 hours.

The reaction mixture was allowed to cool, milled and washed with acetone/methanol (30/70) and water. The resulting polymer was dried in an air oven at 120°C.

Example 12

25

The polymerisation procedure of Example 11 was followed, except that the ratio of 4,4'-dihydroxybiphenyl to 4,4'-dihydroxydiphenylsulphone was 1:2. The polymer has a Tg of 198°C and on RV of 0.52.

30

Example 13 - Sulphonation of Polymers of Examples 1 to 12

The polymers of Examples 1 to 12 were sulphonated by stirring each polymer in 98% sulphuric acid (3.84g polymer/100g sulphuric acid) for 21 hours at 50°C. Thereafter, the reaction solution was allowed to drip into stirred deionised water. Sulphonated polymer precipitated as free-flowing beads. Recovery was by filtration, followed by washing with deionised water until the pH was neutral and subsequent drying. In general, <sup>1</sup>H nmr in DMSO-d<sub>6</sub> confirmed that 100 mole% of the biphenyl units had sulphonated, giving one sulphonic acid group, ortho to the ether linkage, on each of the two aromatic rings comprising the biphenyl unit. For examples 3 to 5, 100% sulphonation of -O-Ph-Ph-O- moieties was confirmed by converting the sulphonated ionomer from the H<sup>+</sup> form to Na<sup>+</sup> form, by reacting 0.5g of the dry sulphonated copolymer with an aqueous solution of NaOH (2.5g NaOH/200ml water) at 60-65°C for 2 hours then washing the product with water and drying at 60°C, followed by sodium analysis.

Example 14 - Membrane Fabrication

Membranes were produced from selected polymers of Examples 1 to 12 after sulphonation as described in Example 13 by dissolving respective polymers in N-methylpyrrolidone (NMP). The polymers were dissolved at a concentration of 15% wt/v, except for Examples 3a and 6 which were dissolved to 4% wt/v. The homogeneous solutions were cast onto clean glass plates and then drawn down to give 300 micron films, using a stainless steel Gardner Knife. Evaporation at 100°C under vacuum for 24

hours produced membranes of mean thickness 40 microns except that Examples 3a and 6 produced membranes of about 10 microns.

#### 5      Example 15 - Water-uptake of the Membranes

5cm x 5cm x 40 microns samples of membranes of Example 14 were immersed in deionized water (500ml) for 3 days, dried quickly with lint-free paper to remove surface water  
10 and weighed, dried in an oven at 50°C for 1 day, allowed to cool to ambient temperature in a desiccator then weighed quickly.

The water uptake was measured as follows, with the  
15 results being provided in the table below. "Equivalent weight" is defined as the weight of polymer containing unit weight of replaceable acidic hydrogen.

$$\% \text{ Water Up-take} = \frac{\text{Wet Weight} - \text{Dry Weight}}{\text{Dry Weight}} \times 100$$

20

Dry Weight		
Membrane - prepared from sulphonated polymer of Example No:	Equivalent Weight (g/mol)	% Water Up-take
2	360	136.4
3a	458	54.4
6	419	69.3
7a	476	61.5
8	690	30.5
9	904	21.9
10	583	38.7
11	976	21.6
12	744	30.7

Example 16 - Performance of membranes in a Polymer Electrolyte Membrane Fuel Cell

The membranes prepared from sulphonated polymers of Examples 8 to 11 were installed in a Standard PEMFC single cell test module and polarisation data was generated and compared to Nafion 115, a leading commercially-available membrane. The current densities obtained at 0.8V were 0.42, 0.35, 0.58 and 0.26 Acm<sup>-2</sup> for the Example 8 to 11 polymers respectively, compared to 0.12 Acm<sup>-2</sup> for Nafion 115.

Example 17

The S number of a polymer is defined as follows:

$$S \text{ Number} = \frac{\text{Number of unsulphonated phenyls}}{\text{Number of sulphonated phenyls}}$$

The S number for polymers described above is summarised in the table below.

Example No.	S Number
1	2.33
2	2
3	3
4	5
5	7
6	2.6
7a	3
8	5
9	7
10	4



11	7
12	5

#### Example 18

A 500ml, 3-necked round-bottomed flask fitted with a stirrer, nitrogen inlet and air condenser was charged with 4,4'-difluorobenzophenone (35.79g, 0.164 mole), hydroquinone (11.01g, 0.10 mole), 4,4'-dihydroxybiphenyl (18.62g, 0.10 mole), 4,4'-bis(4-chlorophenylsulphonyl)biphenyl (LCDC) (20.13g, 0.04 mole) and diphenylsulphone (202.76g) and the contents were heated under a nitrogen blanket to 160°C to form a nearly colourless solution. While maintaining a nitrogen blanket, anhydrous potassium carbonate (29.02g, 0.21 mole) was added and the mixture stirred for 35 minutes. The temperature was raised gradually to 220°C over 2 hours then raised to 280°C over 2 hours and maintained for 2 hours.

The reaction mixture was allowed to cool, milled and washed with acetone/methanol and water. The resulting solid polymer was dried at 140°C under vacuum. The polymer had a reduced viscosity of (RV) 2.50 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84g.cm<sup>-3</sup>, said solution containing 1g of polymer/100cm<sup>3</sup>) and a Tg of 186°C.

#### Example 19

A 250ml, 3-necked round-bottomed flask fitted with stirrer, nitrogen inlet and air condenser was charged with 4,4'-difluorobenzophenone (33.06g, 0.1515 mole),

hydroquinone (13.21g, 0.12 mole), 9,9'-bis(4-hydroxyphenyl)fluorene (HPF) (10.512g, 0.03 mole), and diphenylsulphone (100.93g) and the contents were heated under a nitrogen blanket to 150°C to form a nearly  
5 colourless solution. While maintaining a nitrogen blanket, anhydrous potassium carbonate (21.77g, 0.15751 mole) was added. The temperature was raised to 175°C maintained for 2 hours, raised to 200°C maintained for 50 minutes, raised to 250°C maintained for 45 minutes, raised to 300°C  
10 maintained for 90 minutes.

The reaction mixture was allowed to cool, milled and washed with acetone/methanol and water. The resulting solid polymer was dried at 140°C under vacuum. The polymer  
15 had an reduced viscosity (RV) of 0.76 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84g.cm<sup>-3</sup>, said solution containing 1g of polymer/100cm<sup>3</sup>) and a Tg of 165°C.

20 n Example 20

A 250ml, 3-necked round-bottomed flask fitted with a stirrer, nitrogen inlet and air condenser was charged with 4,4'-bis(4-chlorophenylsulphonyl)-terphenyl (23.2g, 0.04  
25 mole), 4,4'-dihydroxybiphenyl (7.44g, 0.040 mole) and diphenylsulphone (80g) and the contents were heated under a nitrogen blanket to 170°C to form a nearly colourless solution. While maintaining a nitrogen blanket, anhydrous potassium carbonate (5.64g, 0.408 mole) was added. The  
30 temperature was raised to 200°C and maintained for 30 minutes, raised to 250°C and maintained for 15 minutes, raised to 275°C and maintained for 15 minutes, raised to 330°C and maintained for 1 hour.

The reaction mixture was allowed to cool, milled and washed with acetone/methanol and water. The resulting solid polymer was dried at 140°C under vacuum. The polymer  
5 had an inherent viscosity (IV) of 0.50 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84g.cm<sup>-3</sup>, said solution containing 0.1g of polymer/100cm<sup>3</sup>) and a Tg of 264°C.

10      Example 21

A 250ml, 3-necked round-bottomed flask fitted with a stirrer, nitrogen inlet and air condenser was charged with 4,4'-difluorobenzophenone (21.82g, 0.10 mole), 4,4'-  
15 dihydroxybiphenyl (18.62g, 0.10 mole) and diphenylsulphone (60g) and the contents were heated under a nitrogen blanket to 180°C to form a nearly colourless solution. While maintaining a nitrogen blanket anhydrous potassium carbonate (14.10g, 0.102 mole) was added. The temperature  
20 was raised to 200°C over 60 minutes, raised to 250°C maintained for 5 mins, raised to 325°C maintained for 5 mins, raised to 370°C over 90 mins, maintained for 10 mins.

The reaction mixture was allowed to cool, milled and  
25 washed with acetone/methanol and water. The resulting solid polymer was dried at 140°C under vacuum. The polymer had an inherent viscosity (RV) of 1.28 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84g.cm<sup>-3</sup>, said solution containing 1g of  
30 polymer/100cm<sup>3</sup>) and a Tg 167°C.

Example 22

A 250ml, 3-necked round-bottomed flask fitted with a stirrer, nitrogen inlet and air condenser was charged with 4,4'-difluorobenzophenone (22.04g, 0.101 mole), 4,4'-dihydroxybiphenyl (6.52g, 0.035 mole), hydroquinone (7.16g, 0.065 mole) and diphenylsulphone (60g) and the contents were heated under a nitrogen blanket to 180°C to form a nearly colourless solution. While maintaining a nitrogen blanket anhydrous sodium carbonate (10.60g, 0.100 mole) and anhydrous potassium carbonate (0.28g, 0.002 mole) were added. The temperature was raised to 200°C held for 1 hour, raised to 250°C held for 1 hour, raised to 300°C held for 1 hour. The reaction mixture was allowed to cool, milled and washed with acetone/methanol and water. The resulting solid polymer was dried at 140°C under vacuum. The polymer has an inherent viscosity (IV) 0.92 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84 g.cm<sup>-3</sup>, said solution containing 0.1 g of polymer/100cm<sup>3</sup>) and a Tg 156°C.

#### Example 23

A 250ml, 3-necked round-bottomed flask fitted with a stirrer, nitrogen inlet and air condenser was charged with 4,4'-bis(4-fluorobenzoyl)diphenylether (21.34g, 0.515 mole), 4,4'-dihydroxybiphenyl (9.31g, 0.050 mole) and diphenylsulphone (90g) and the contents were heated under a nitrogen blanket to 160°C to form a nearly colourless solution. While maintaining a nitrogen blanket anhydrous sodium carbonate (5.30g, 0.050 mole) and anhydrous potassium carbonate (0.14g, 0.001 mole) were added. The temperature was raised at 1°C/min until it reached 345°C and held for 1 hour.

The reaction mixture was allowed to cool, milled and washed with acetone/methanol and water. The resulting solid polymer was dried at 140°C under vacuum. The polymer had an inherent viscosity (RV) 1.48 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84g.cm<sup>-3</sup>, said solution containing 1g of polymer/100cm<sup>3</sup>) and a Tg 163°C.

Example 24 - General procedure for Sulphonation of Polymers of Examples 18 to 23

The polymers prepared as described in Examples 18 to 23 were sulphonated according to the following procedure.

The dried polymer was placed in a three-necked round-bottomed flask fitted with a stirrer containing 98% concentrated sulphuric acid (100cm<sup>3</sup>), heated with stirring to 60°C and maintained at the temperature for 3 hours. The reaction product was poured into 5 litres of stirred ice/water mixture. The product precipitated out. It was then filtered-off, washed with iced-water until the pH was neutral, washed with methanol and dried under vacuum at 100°C. The degree of sulphonation was determined by elemental analysis, filtration or Nmr.

Example 25 - Sulphonation of polymer of Example 22

The dried polymer from Example 22 (10g) was placed in a three-necked round-bottomed flask fitted with a stirrer, containing 98% concentrated sulphuric acid (100cm<sup>3</sup>), heated

with stirring to 60°C and maintained at that temperature for 3 hours. The reaction products was poured into 5 litres of stirred ice/water mixture. The product precipitated out, was filtered-off, washed with iced-water until the pH was neutral, washed with methanol and dried under vacuum at 100°C. Nmr analysis showed the polymer had readily sulphonated, in which 95-100 mole% of the ether-diphenyl-ether and ether-phenyl-ether units had been sulphonated.

#### Example 26

A 500ml 3-necked round bottomed quickfit flask fitted with stirrer/stirrer guide, nitrogen inlet and outlet was charged with 4,4'-difluorobenzophenone (22.04g, 0.102 mole), 4,4'-dihydroxybenzophenone (10.71g, 0.05 mole), 2,7-dihydroxynaphthalene (8.01g, 0.05 mole) and diphenyl sulphone (76.9g) and purged with nitrogen for at least 1 hour. The contents were heated under a nitrogen blanket to about 132°C to form a clear solution. While maintaining a nitrogen blanket, dried sodium carbonate (10.81g, 0.102 mole) was added. The temperature was raised gradually to 290°C over 240 minutes then maintained for 65 minutes.

The reaction mixture was allowed to cool, milled and washed with acetone and water. The resulting polymer had a Tg of 158°C and melt viscosity at 400°C, 1000sec<sup>-1</sup> of 0.5 kNsm<sup>-2</sup>.

The polymer was sulphonated using the process described in Example 13. The resultant sulphonated

polymer has a water-uptake of 69.3% and an equivalent weight of 445.

5 The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

10

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except 15 combinations where at least some of such features and/or steps are mutually exclusive.

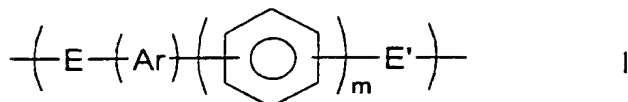
Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be 20 replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

25

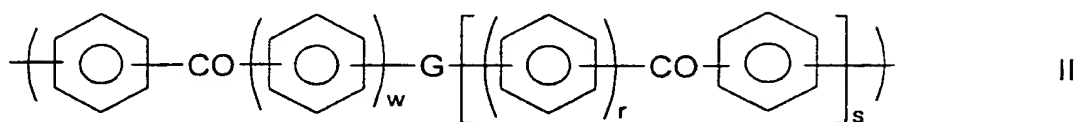
The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying 30 claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

## CLAIMS

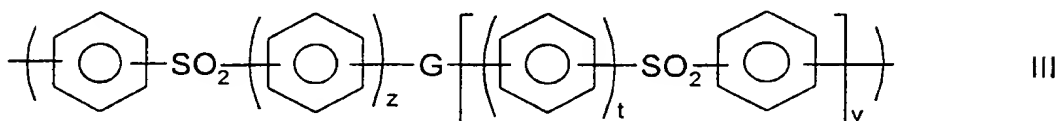
1. A polymer electrolyte membrane which includes a  
 5 polymer having a moiety of formula



and/or a moiety of formula

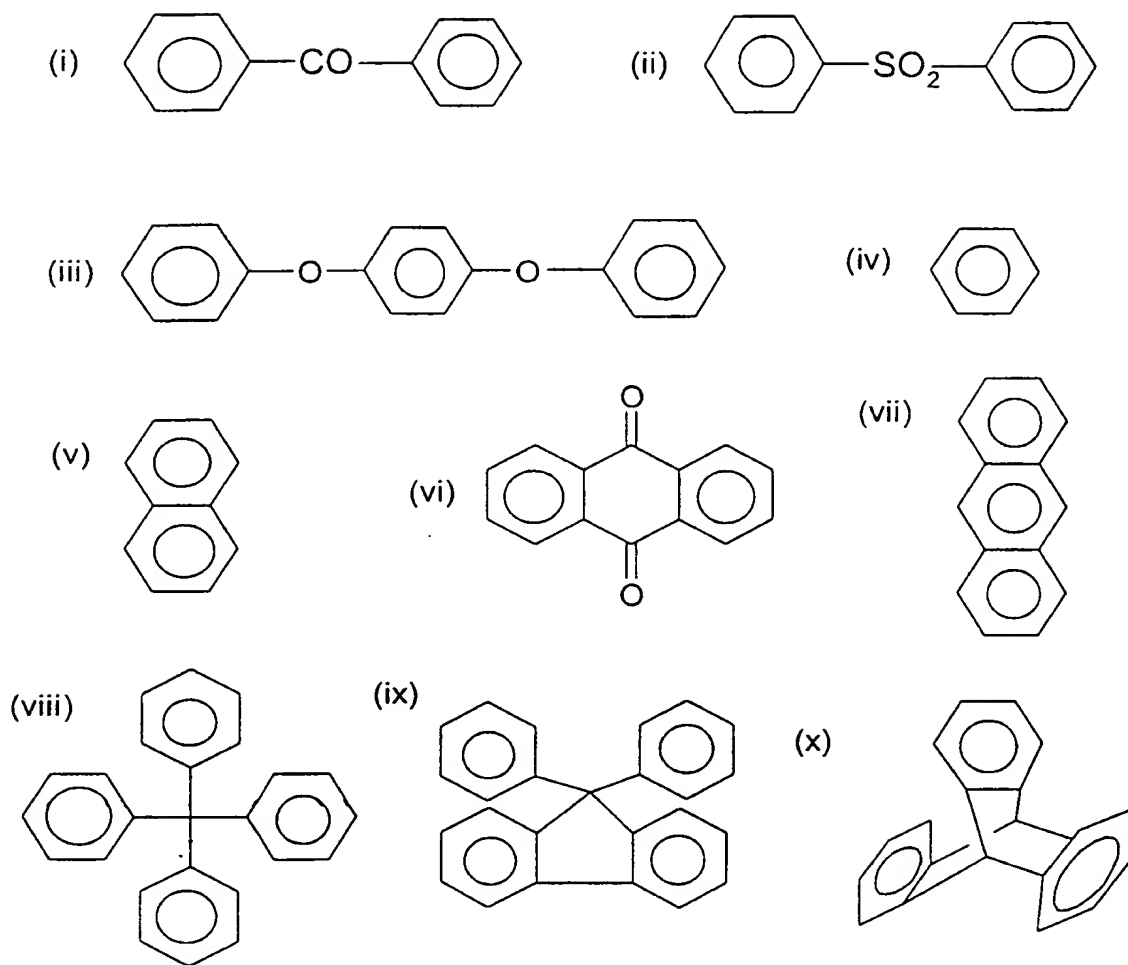


- 10 and/or a moiety of formula



wherein at least some of the units I, II, and/or III are sulphonated; wherein the phenyl moieties in units I, II and III are independently optionally substituted and  
 15 optionally cross-linked; and wherein m, r, s, t, v, w and z independently represent zero or a positive integer, E and E' independently represent an oxygen or a sulphur atom or a direct link, G represents an oxygen or a sulphur atom, a direct link or a -O-Ph-O- moiety where Ph represents a  
 20 phenyl group and Ar is selected from one of the following moieties (i) to (x) which is bonded via one or more of its phenyl moieties to adjacent moieties





2. A polymer electrolyte membrane which includes a polymer having a moiety of formula I and/or a moiety of formula II and/or a moiety of formula III as described in claim 1, wherein at least some of units I, II and/or III are functionalized to provide ion exchange sites.

3. A membrane according to claim 1 or claim 2, wherein said polymer is crystalline.

4. A membrane according to any preceding claim, wherein "a" represents the mole % of units of formula I in said

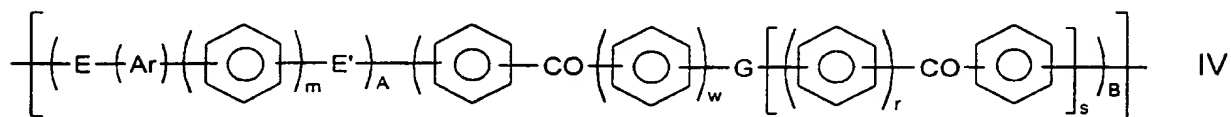
polymer; "b" represents the mole % of units of formula II in said polymer; and "c" represents the mole % of units of formula III in said polymer and wherein a is in the range 45-100 and the sum of b and c is in the range of 0-55.

5

5. A membrane according to any preceding claim, wherein said polymer consists essentially of moieties I, II and/or III.

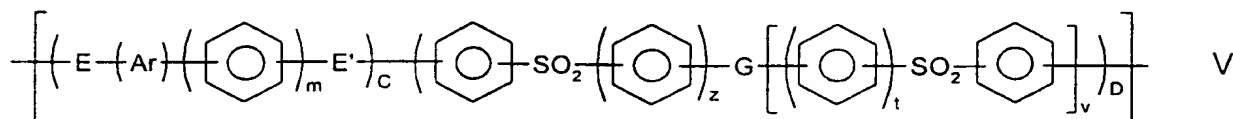
10

6. A membrane according to any preceding claim, wherein said polymer is a homopolymer having a repeat unit of general formula



15

or a homopolymer having a repeat unit of general formula



or a random or block copolymer of at least two different units of IV and/or V

20

wherein A, B, C and D independently represent 0 or 1.

7. A membrane according to claim 6, wherein said polymer includes at least one repeat unit of formula IV.

25

8. A membrane according to claim 6, wherein said polymer is a copolymer comprising a first repeat unit of formula

IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, w represents 1, s represents zero, A and B represent 1; and

5

a second repeat unit of formula V wherein E and E' represent oxygen atoms, Ar represents a structure (i), m represents 0, C represents 1, z represents 1, G represents a direct link, v represents 0 and D represents 1.

10

9. A membrane according to claim 6, wherein said polymer is a copolymer comprising a first repeat unit of formula IV, wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, w represents 1, s represents 0, A and B represent 1.

10. A membrane according to claim 6, wherein said polymer is a copolymer comprising a first repeat unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, w represents 1, s represents 0, A and B represent 1; and a second repeat unit of formula IV wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (i), m represents zero, A represents 1, B represents 0.

11. A membrane according to claim 6, wherein said polymer is a copolymer comprising a first repeat unit which is either:

(a') of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a

moiety of structure (iv), m and s represent zero, w represents 1 and A and B represent 1; or

(b') of formula IV wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (i), m represents zero, A represents 1, B represents zero;

and a second repeat unit which is either:

10

(c') of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, w represents 1, s represents zero, A and B represent 1; or

15

(d') of formula IV wherein E represents an oxygen atom, E' is a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represents 1, A and B represent 1.

20

12. A membrane according to claim 11, wherein said polymer has a repeat unit as described in paragraph (a') or (b') in combination with a repeat unit as described in paragraph (c').

25

13. A membrane according to claim 6, comprising a first repeat unit which is selected from the following:

(a) a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represents 1 and A and B represent 1;

30

(b) a unit of formula IV wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (i), m represents zero, A represents 1, B represents zero;

5

(c) a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and v represent zero, z represents 1 and C and D represent 1;

10

(d) a unit of formula V wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (ii), m represents 0, C represents 1, D represents 0; or

15

(e) a unit of formula V wherein E and E' represents an oxygen atom, Ar represents a structure (i), m represents 0, C represents 1, Z represents 1, G represents a direct link, v represents 0 and D represents 1;

20

and a second repeat unit which is selected from the following:

(f) a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, w represents 1, s represents zero, A and B represent 1;

(g) a unit of formula IV wherein E represents an oxygen atom, E' is a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represent 1, A and B represent 1;

30

(h) a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, z represents 1, v represents 0, C and D represent 1; and

5

(i) a unit of formula V wherein E represents an oxygen atom, E' represents a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and v represent zero, z represents 1, C and D represent 1;

10

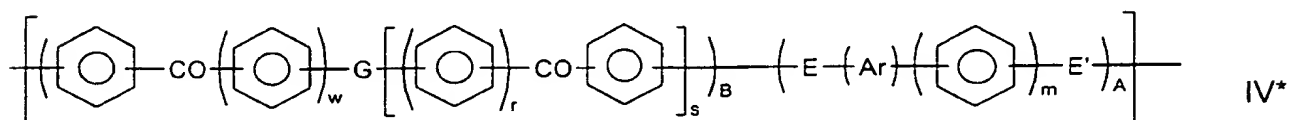
14. A membrane according to any of claims 6 to 13, wherein said second unit is selected from a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (v), m represents 0, w represents 1, s represents 0, A and B represent 1; or a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (v), m represents 0, z represents 1, v represents 0, c and d represent 1.

20

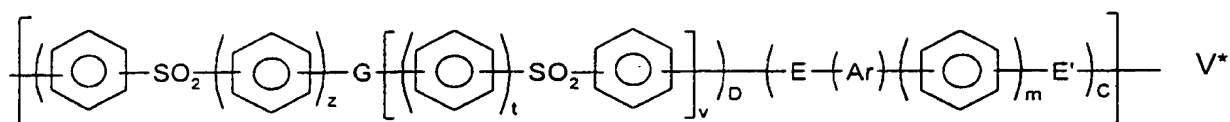
15. A membrane according to claim 13 or claim 14, wherein said copolymer has a first repeat unit selected from units (b), (d) or (e) in combination with a second repeat unit selected from units (f) or (h).

25

16. A membrane according to any of claims 1 to 5, wherein said polymer is a homopolymer having a repeat unit of general formula



or a homopolymer having a repeat unit of general formula



5 or a random or block copolymer of at least two different units of IV\* and/or V\* wherein A, B, C and D independently represent 0 or 1.

17. A membrane according to claim 16, wherein said  
 10 polymer includes: a repeat unit of formula IV\* wherein E represents a direct link, E' represents an oxygen atom, G represents a direct link, w, s and m represent 0, A and B represent 1; and/or a repeat unit of formula V\* wherein E represents a direct link, E' represents an oxygen atom, G  
 15 represents a direct link, z, v and m represent 0, C and D represent 1.

18. A membrane according to claim 17 which includes a repeat unit of formula IV\* or V\* and any of units (a) to  
 20 (i) according to claim 13.

19. A membrane according to any preceding claim, wherein said polymer includes at least some ketone moieties in the polymeric chain.

25

20. A membrane according to any preceding claim, wherein said polymer includes a biphenylene moiety.

21. A membrane according to any preceding claim, wherein said polymer includes a -O-biphenylene-O- moiety.

22. A membrane according to any preceding claim, wherein  
5 said polymer includes a -O-naphthalene-O-moiety.

23. A membrane according to any preceding claim, wherein said polymer has a glass transition temperature (T<sub>g</sub>) of at least 144°C.

10

24. A membrane according to claim 23, wherein said glass transition temperature is at least 154°C.

25. A membrane according to any preceding claim, wherein  
15 said polymer has an inherent viscosity of at least 0.3.

26. A membrane according to any preceding claim, for a fuel cell.

20 27. A membrane according to any preceding claim, for an electrolyser.

28. A fuel cell incorporating a polymer electrolyte membrane according to any of claims 1 to 25..

25

29. An electrolyser incorporating a polymer electrolyte membrane according to any of claims 1 to 25.

30. A gas diffusion electrode incorporating a polymer  
30 electrolyte membrane according to any of claims 1 to 25.

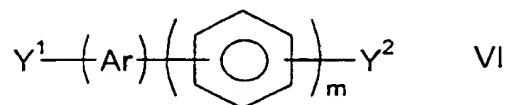
31. A novel polymer as described in any of claims 1 to 25 *per se*.



32. A process for the preparation of a polymer as described in any of claims 1 to 25, the process comprising:

5

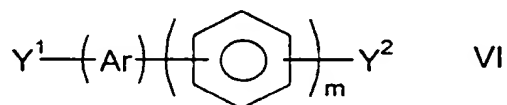
(a) polycondensing a compound of general formula



with itself wherein  $Y^1$  represents a halogen atom or a group -EH and  $Y^2$  represents a halogen atom or, if  $Y^1$  represents a halogen atom,  $Y^2$  represents a group E'H; or

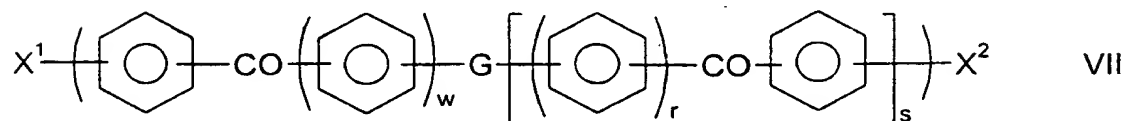
10

(b) polycondensing a compound of general formula

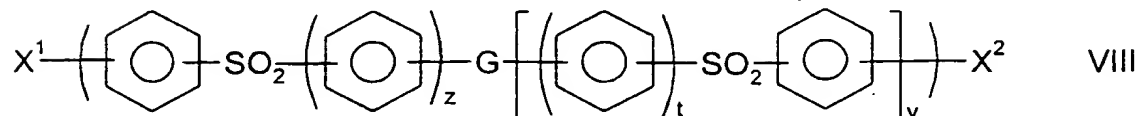


15

with a compound of formula



and/or with a compound of formula



wherein  $Y^1$  represents a halogen atom or a group -EH (or -E'H if appropriate) and  $Y^2$  represents a halogen atom or a group -E'H and  $X^2$  represents the other one of a halogen atom or a group -E'H (or EH of appropriate); and

(c) optionally copolymerizing a product of a process as described in paragraph (a) with a product of a process as described in paragraph (b);

10

wherein the phenyl moieties of units VI, VII and/or VIII are optionally substituted; the compounds VI, VII and/or VIII are optionally sulphonated; and Ar, m, w, r, s, z, t, v, G, E and E' are as described in any of claims 1 to 20 except that E and E' do not represent a direct link; the process also optionally comprising sulphonating and/or cross-linking a product of the reaction described in paragraphs (a), (b) and/or (c) to prepare said polymer.

20 33. A process according to claim 31, wherein sulphonation is carried out in concentrated sulphuric acid at an elevated temperature.

34. A novel polymer as described in any of claims 1 to 24 (except that the polymer is not sulphonated) *per se*.

25 35. A membrane, a fuel cell, a process, a novel polymer, each being independently substantially as hereinbefore described, with reference to the examples.

1/1

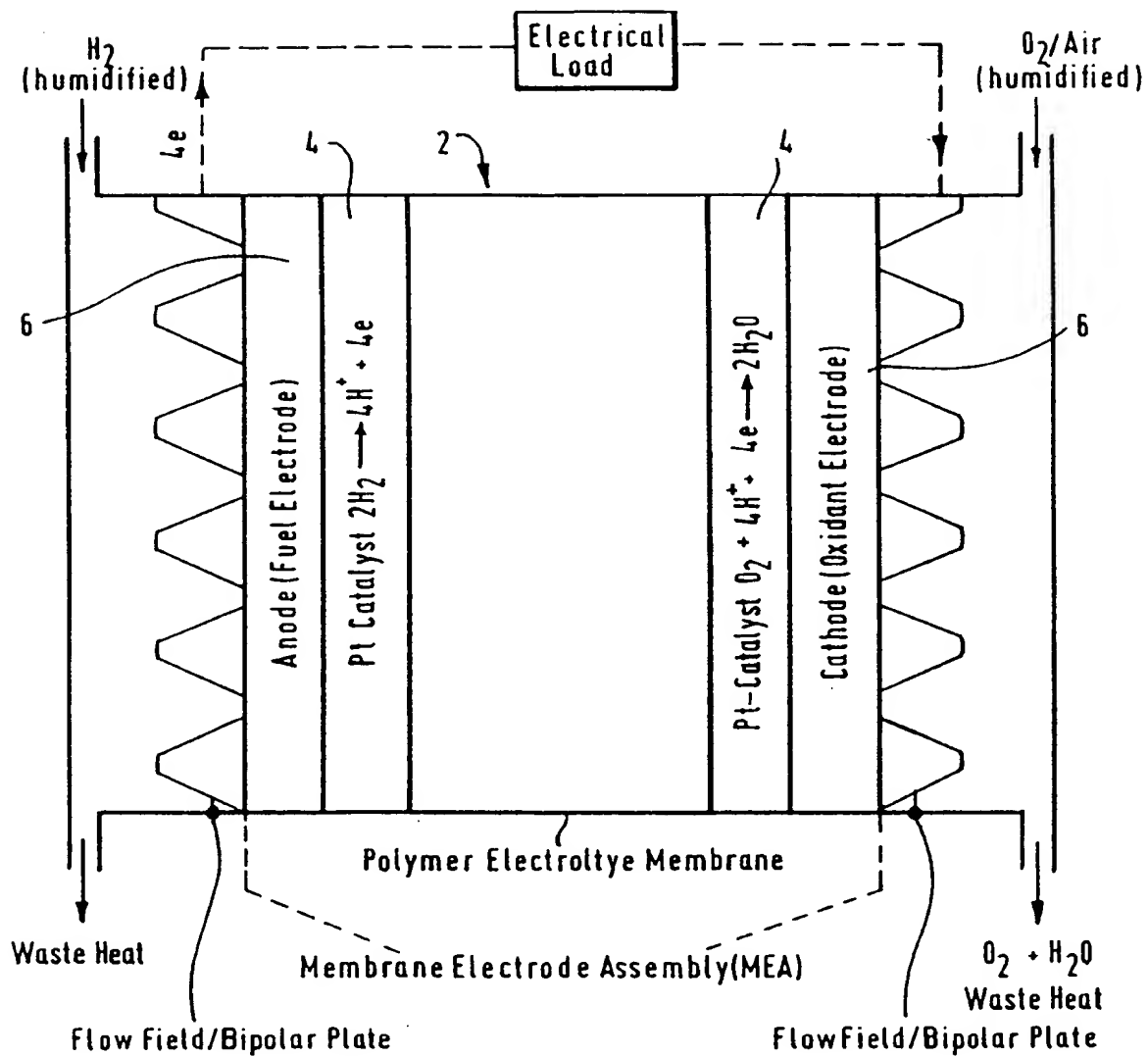


FIG.1.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 99/02833

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G65/48 C08J5/22 H01M6/18 H01M10/40 H01M8/10  
H01M2/16

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C08J H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 574 791 A (HOECHST AG) 22 December 1993 (1993-12-22) cited in the application claims 1-19 page 7, line 35 - line 45 ---	1-35
X	WO 96 29360 A (CLAUSS JOACHIM ;DECKERS GREGOR (DE); HOECHST AG (DE); WITTELER HEL) 26 September 1996 (1996-09-26) cited in the application claims 1-30 *Structure (III)* page 7 ---	1-35
X	EP 0 382 440 A (ICI PLC) 16 August 1990 (1990-08-16) claims 1,2 ---	1-7, 16, 19, 34, 35
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*Z\* document member of the same patent family

Date of the actual completion of the international search

3 December 1999

Date of mailing of the international search report

17. 01. 2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

O'Sullivan, T

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/02833

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 748 485 A (COMMISSARIAT ENERGIE ATOMIQUE) 14 November 1997 (1997-11-14) claim 1; example 1 page 16, line 1 - line 6 ---	1-3, 19-31
X	EP 0 008 895 A (ICI PLC) 19 March 1980 (1980-03-19) cited in the application claim 1 example 1 page 4, line 22 - line 30 ---	32,33
X	EP 0 211 693 A (UNION CARBIDE CORP) 25 February 1987 (1987-02-25) column 11 -column 14 ---	32-34
P,X	EP 0 932 213 A (SUMITOMO CHEMICAL CO) 28 July 1999 (1999-07-28) claims 1,3 -----	1-35

## INTERNATIONAL SEARCH REPORT

In. ational application No.  
PCT/GB 99/02833

### Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1-35 (all in part)  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

### Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

#### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/GB 99/02833

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-35 (all in part)

Present claims 1-35 relate to an extremely large number of possible polymer types. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the polymers claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the polyarylether ketones or polyarylether sulphones described in the examples of the present application.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PC1, AB 99/02833

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0574791 A	22-12-1993	CA 2098238 A	14-12-1993
		JP 6093114 A	05-04-1994
		US 5438082 A	01-08-1995
		US 5741408 A	21-04-1998
		US 5561202 A	01-10-1996
WO 9629360 A	26-09-1996	DE 19510026 A	26-09-1996
		DE 19545642 A	12-06-1997
		DE 19548423 A	26-06-1997
		DE 19610303 A	25-09-1997
		CA 2215911 A	26-09-1996
		EP 0815160 A	07-01-1998
		JP 11502249 T	23-02-1999
EP 0382440 A	16-08-1990	AU 4907490 A	16-08-1990
		CA 2009323 A	08-08-1990
		JP 3014841 A	23-01-1991
FR 2748485 A	14-11-1997	CA 2254086 A	13-11-1997
		EP 0897407 A	24-02-1999
		WO 9742253 A	13-11-1997
EP 0008895 A	19-03-1980	EP 0008894 A	19-03-1980
		EP 0029633 A	03-06-1981
		JP 1512209 C	09-08-1989
		JP 55036296 A	13-03-1980
		JP 63051174 B	13-10-1988
		JP 1390886 C	23-07-1987
		JP 55048222 A	05-04-1980
		JP 61036781 B	20-08-1986
		JP 1650209 C	30-03-1992
		JP 3012094 B	19-02-1991
		JP 62089730 A	24-04-1987
		JP 1584173 C	22-10-1990
		JP 59074128 A	26-04-1984
		JP 62028169 B	18-06-1987
		JP 1594860 C	27-12-1990
		JP 2017571 B	20-04-1990
		JP 61043630 A	03-03-1986
		US 4273903 A	16-06-1981
		US 4268650 A	19-05-1981
EP 0211693 A	25-02-1987	CA 1257740 A	18-07-1989
		JP 62116628 A	28-05-1987
		US 4774311 A	27-09-1988
EP 0932213 A	28-07-1999	NONE	